A TEXTBOOK OF

MODERN ORGANIC CHEMISTRY

JAGINDAR SINGH

West Bengal

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A TEXTBOOK OF

MODERN ORGANIC CHEMISTRY

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COVERING THE SYLLABI FOR THE THREE-YEAR DEGREE AND HONOURS COURSES

by

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WITH AN INTRODUCTION

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NEW
(ELEVENTH)
EDITION
Greatly Improved, Amplified & Brought Up-to-date

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PREFACE TO THE ELEVENTH EDITION

The revision of the text for this new edition of Modern Organic Chemistry had to be very thorough because of the need for bringing the book in line with the newly introduced syllabi of various Universities for the three-year degree course. Besides numerous minor changes and additions, a new chapter on Electronic Theory of Aromatic Substitution has been added. The chapters dealing with Terpenes and Physical Properties and Chemical Constitution have been considerably amplified. Another noteworthy addition is a comprehensive appendix dealing with the more important petrochemicals, a subject of the greatest importance at the present time.

Our thanks are due to all friends, professors as well as students, who have so kindly given their valuable suggestions for the improvement of the text, particularly Dr. S. A. Faseeh of University Institute of Chemistry, Lahore (Pakistan) and Prof. Sujan Singh of Government College, Ajmer.

Delhi *JAGINDAR SINGH*
August 1, 1964 *N. S. SEKHON*

CONTENTS

CHAPTER | PAGE

Introduction 1

PART I

ORGANIC ANALYSIS AND GENERAL THEORY

1. Methods of Purification and Criteria of Purity 7
2. Qualitative Elementary Analysis 28
3. Quantitative Elementary Analysis 33
4. Determination of Empirical and Molecular Formulæ 46
5. Molecular Structure and Isomerism 63
6. Relation between Physical Properties and Chemical Constitution 82
7. Stereochemistry 104
8. Catalytic Organic Reactions 125

PART II

ALIPHATIC OR OPEN-CHAIN COMPOUNDS

9. Alkanes 132
10. Unsaturated Hydrocarbons 152
11. Petroleum Industry 179
12. Halogen Derivatives of Hydrocarbons 194
13. Organo-Metallic Compounds 215
14. Monohydric Alcohols 224
15. Esters of Inorganic Oxy-acids 252
16. Ethers 257
17. Aldehydes and Ketones 265
18. Monocarboxylic Acids 299
19. Derivatives of Monocarboxylic Acids 322
20. Halogen-substituted monocarboxylic Acids 339
21. Polyhydric Alcohols 343
22. Fats, Fatty Oils and Detergents 358
23. Dicarboxylic Acids 373
24. Hydroxycarboxylic Acids 393
25. Carbonic Acid and its Derivatives 409
26. Aldehydic and Ketonic Acids 417
27. Cyanogen Compounds 425
28. Alkyl Compounds of Sulphur and Arsenic 435
29. Nitroparaffins and Alkyl Nitrites 443
30. Amines and Quartenary Ammonium Derivatives 447
31. Amino Acids 461
32. Proteins 470
33. Ureides and Purines 475
34. Carbohydrates 485

PART III

CYCLIC OR CLOSED CHAIN COMPOUNDS

35. Alicyclic Compounds 531
36. Introduction to Aromatic Series 539
37. Benzene 546
38. Homologues of Benzene 558
39. Substitution in Benzene Nucleus 563
40. Electronic Theory of Aromatic Substitution 574
41. Aromatic Halogen Compounds 579
42. Aromatic Nitro Compounds 588
43. Aromatic Amino Compounds 598
44. Diazonium Salts and Related Compounds 615
45. Aromatic Sulphonic Acids 630
46. Aromatic Arsenic Compounds 634
47. Phenols 636
48. Quinones 649
49. Aromatic Alcohols, Aldehydes and Ketones 652
50. Aromatic Acids 662
51. Polyphenyl Compounds 679
52. Naphthalene and its Derivatives 686
53. Anthracene and its Derivatives: Phenanthrene 695
54. Uninuclear Hetrocyclic Compounds 703
55. Heterocyclic Compounds Containing Condensed Nuclei 712
56. Alkaloids 722
57. Terpenes 733

APPENDIX :

I. Some Important Petrochemicals 750

INDEX 763

LIST OF PLATES :—

I. Camellia thea : Coffea arabica (*Facing page*) 481
II. Datura stramonium : Atropa belladonna (*Facing page*) 728
III. Papaver somniferum : Cinchona officinalis (*Facing page*) 731

A TEXTBOOK OF
MODERN ORGANIC CHEMISTRY

INTRODUCTION

By BAWA KARTAR SINGH, M.A., Sc.D., F.I.C., I.E.S.

1. Rise of Organic Chemistry.—The scientific foundation of organic chemistry may be said to date from 1832 when Leibig and Wöhler published their classical investigation on the *Radical of Benzoic Acid.* The position of organic chemistry at the time may be understood from a letter written in 1837 by Wöhler to Berzelius in which he says: "It seems to me like the tropical forest, primeval, full of the strangest growths, an endless and pathless thicket, in which a man may well dread to wander." It is not implied that before this time no organic compounds were known. In fact, as early as the second half of the 17th century, chemical substances had been classified according to their origin from "the three kingdoms of Nature" by Nicolas Lemery in the famous *Cours de Chymie* (1675) under the following three divisions:

(1) *Mineral substances*—such as metals, minerals, earth and stones.

(2) *Vegetable substances*—such as plants, resins, gums, fruits, juices and honey.

(3) *Animal substances*—such as various parts of the animal body and excrements.

This is, thus, the first attempt to separate organic from inorganic chemistry.

The exact composition of chemical substances was not known at that time, although Stahl (1660—1734) pointed out the preponderance of what he called the "aqueous and combustible principles" (hydrogen and carbon) in substances of vegetable and animal origin. Scheele (1742—86) had isolated and studied many of the commoner organic acids and had discovered glycerine (1779), obtained by heating olive oil with litharge. Rouelle (1703–70) had discovered, among other substances, urea and hippuric acid. Many other organic products have been discovered, but no real advance was possible until the foundation of *Atomic Theory* by Dalton (about 1803). Berzelius (1779—1848), the great Sweedish chemist, whose classical work on the atomic weights of elements must always rank high for its accuracy, greatly improved the methods of organic analysis, *i.e.*, the methods for the determination of carbon, hydrogen, and nitrogen in organic substances. He further proved by his accurate analyses, especially of the salts of organic acids, that both in their composition and in the products of their decomposition, these substances followed the same fundamental laws of chemical combination as held for inorganic substances. This development was continued by Liebig who in 1831, introduced and improved adequate methods of organic analysis. Organic chemistry thus began to assume the status of an exact science. Organic compounds, like inorganic substances, could also be represented by means of molecular formulae. This development was also largely due to Lavoisier (1743—94) who undertook the study of the composition of chemical substances. He found that most of the vegetable substances were built up of carbon, hydrogen and oxygen, and that these three elements, generally accompanied by nitrogen and sometimes by phosphorus and sulphur, were present in all substances of animal origin. He proved by direct experiment that organic substances had definite composition, and thus, recognized the fact that the general laws of chemical combination were equally applicable to all substances, irrespective of their origin or the degree of their complexity. In spite of the above mentioned similarity found in organic and inorganic compounds, a sharp line of demarcation was drawn between the two groups as regards their synthesis by Berzelius and others. They pointed out that whereas inorganic substances could be synthesised from their constituent elements in the laboratory, this was not possible for organic compounds. It was imagined that a mysterious force of Nature was required for the synthesis of organic products and that it was beyond the power of the chemist to call this *vital force* into play. There was ample reason, too, at the time for this belief, based on the fact that such products had not so far been synthesised in the laboratory. The real reason for this failure to achieve the artificial production of such substances lay both in the complexity of organic products and the rudimentary state of synthetic chemistry at that time. As a result of this, the idea of a vital force remained for many years the barrier between organic and inorganic chemistry. Wöhler's synthesis of urea from ammonium cyanate and Hennel's preparation of alcohol from ethylene, both effected in 1828 in the laboratory, shook the belief in the vital force theory. An ever-growing number of organic syntheses of plant products, such as alizarin and indigo, as well as of many products of animal origin, such as uric acid, gave a death-blow to the "Vital Force Theory of Berzelius."*

2. Main differences between Organic and Inorganic Chemistry.— As a result of the improvements effected in organic analysis by

---

*Nevertheless the "Vital Force" theory was right in one sense : There are many plant and animal products, such as, for instance, proteins, which we are unable to produce artificially. It must be admitted also that we are unable to reproduce Nature's methods and that our methods, compared with hers, are clumsy and uneconomical. It is, however, certain, that in the not far distant future Biochemistry, which may be defined as the chemistry of life, may develop to the same degree of perfection as synthetic organic chemistry. When this is the case, we shall be able to imitate Nature as we can now do, in some cases, by employing her tools as, for example, in the conversion of a sugar into alcohol by means of an enzyme.

Berzelius, and more especially by Liebig (1831), it was established by Lavoisier and others that organic compounds were composed of carbon combined with about half a dozen other elements, of which hydrogen, oxygen and nitrogen were predominant. In this respect, these organic compounds stand in marked contrast to inorganic compounds. It is unusual to find more than three or four inorganic compounds built up from the same three elements, whereas a practically unlimited number of organic compounds may be derived from carbon, hydrogen and oxygen. This is due to the remarkable capacity of carbon for combining with itself. Thus, compounds are known in which as many as sixty carbon atoms are directly united to each other. Though the distinction between organic and inorganic chemistry based on the vital force theory has disappeared, the vast number of known organic compounds—now well over 250,000—which exceeds that of the compounds of all the other elements put together, is a strong argument for treating organic chemistry as a distinct and separate branch of chemistry. The reason is, therefore, purely one of convenience. "Organic Chemistry" is, therefore, best defined as the "Chemistry of the Carbon Compounds", as the element carbon is the invariable constituent of these compounds.

The second point which distinguishes organic from inorganic chemistry is the phenomenon of Isomerism, which is so common in the former. Wöhler's discovery was also important in another way : the doctrine of isomerism was its direct outcome. Wöhler sought to prepare the ammonium salt of cyanic acid ; instead he obtained the highly stable substance, urea : the salt which was first formed in solution passed rapidly over into urea. The elementary composition and molecular formula of the two compounds is the same but they differ in structure : compounds so related are termed *isomeric compounds* or *isomers* and the phenomenon is known as *isomerism* (Berzelius, 1831). Liebig and Wöhler had previously shown (1823) that silver cyanate and silver fulminate were similarly related. Camphor has, at least, 119 known isomers, each containing 78·9 per cent of carbon, 10·5 per cent of hydrogen and 10·5 per cent of oxygen. The molecular formula of these 120 distinct substances is the same, namely $C_{10}H_{16}O$, but the molecular structure and properties are different in each case. The recognition of the principle of isomerism was a great advance in chemical thought and it ultimately led chemists to depict the structure of the isomeric substances as a variable arrangement of the atoms in the molecular edifice. To use an analogy, suppose a wall is to be built of ten black bricks, sixteen red bricks and one white brick, representing the three elements carbon, hydrogen and oxygen respectively. The organic chemist has so far discovered examples of 120 different ways in which these twenty-seven bricks can be arranged. It may be possible to arrange them in other ways, but at least he has the means of distinguishing these 120 different patterns. It is, however, different with most inorganic compounds. One has to be content with a knowledge of their composition only, in other words, with the nature and relative number of the atoms present. Sulphuric acid is represented by the formula H_2SO_4 and that formula represents no other substance.

Thirdly, organic or carbon compounds, as compared with the compounds of other elements, are unstable, and are generally decomposed at high temperatures. This has necessitated the development of special methods and processes of their investigation.

Lastly, organic compounds are much more complex than inorganic compounds ; cane-sugar is represented by the formula $C_{12}H_{22}O_{11}$, and stearin, one of the constituents of mutton fat and lard, by the formula $C_{57}H_{110}O_6$ and the molecules of starch or cellulose may number its component atoms in several thousands ; whereas it is very seldom that the molecular formula of an inorganic substance contains more than a dozen atoms. These considerations clearly show that the treatment of carbon compounds as a separate branch called "Organic Chemistry" is not based on any fundamental difference between the two branches of chemistry. It is the result of recognition of the principle of the division of labour and is guided largely by considerations of convenience of the workers in the two fields.

3. **Organic Chemistry in Service of Chemical Industry.**—The extraordinary development of organic chemistry which has been mentioned in the previous section is due to two main influences. One is the study of the structure of organic compounds which received a great impetus from the laws of Kekule formulated in 1858. These laws are capable not only of co-ordinating and explaining a vast array of known facts included in organic chemistry, but also of predicting new ones with the result that organic chemistry has become almost the most exact of the sciences. If it were alone for these considerations, its development would not have been so great as what we find it today. The other most important influence which has contributed largely in this direction is, however, of economical and technological interest. It was the application of the knowledge of organic chemistry to industry which has had a far-reaching effect in promoting the rapid growth of the science. The large profits which were made by the manufacturer were partly devoted to the advancements of research in technological laboratories and universities. This resulted in the rapid growth of chemical theory, which, in turn reacted on chemical industry. A notable example of successful industrial research is the manufacture of indigo. In 1880, Von Baeyer accomplished the synthesis of indigo in the laboratory. This was taken up by the German dye-stuff industry, which, after seventeen years' strenuous labour and the expenditure of nearly £ 1,000,000, succeeded in establishing the synthesis on a large scale. The high and uniform purity of the synthetic product, coupled with its low price, resulted in the virtual extinction of the indigo-growing industry with dire loss to the European planters of Bihar, and consequent gain to the far-sighted German entrepreneurs who had the initiative and the ability to convert a laboratory experiment into a vast industry.

The position of the drug and medicinal chemical industry has been greatly improved by the introduction of synthetic compounds of therapeutic value, such as, aspirin, phenacetin, salol, sulphonal, antipyrine, salvarsan, saccharin, sulpha drugs and a number of others. Their manufacture is chiefly carried out by German dyestuff industry as an adjunct to the preparation of dyes. As a result of the study of physiological action of synthetically prepared organic compounds, certain typical groups have been recognized as possessing specific narcotic, antiseptic, bacteriostatic or antipyretic actions. Many natural products have been investigated from this point of view, and in many instances as, for example, in the case of the drug cocaine (present in coca leaves), the determination of structure has revealed the particular arrangement of atoms in the molecule, on which the physiological properties of the drug depend. Among the several synthetical products embodying this principle, which were prepared in the laboratory, the simpler novocaine, in the exercise of its particular medicinal functions, has been found more beneficial than the natural material cocaine.

The effect of the application of organic chemistry to industry is, perhaps, best seen in the introduction of synthetic colouring matters. No doubt the art of the dyer was thoroughly known to the ancient civilizations of which we have any knowledge ; the ancient Egyptians, and others were acquainted with the use of mordants and were able to obtain fast shades of colour which have remained permanent for many centuries. But it must be admitted that the number of natural dyes was limited and even as late as the early part of the second half of the nineteenth century indigo, alizarin, extracts of logwood and other woods, safflower, cochineal among the natural dyestuffs, were the chief mainstay of the dyer. The earliest known artificial dye is picric acid, which was obtained from indigo in 1771. It was extensively used as a yellow dye for silk and wool and as a high explosive. In medicine it finds application as an antiseptic and is commonly used as a lotion for burns. The history of modern or synthetic dyes, however, commenced in 1856, when Perkin, at the early age of seventeen, prepared the first aniline dye, Mauve. It was a purely accidental discovery, but Perkin set up a factory at Greenford Green, near London, for its manufacture in the following year. A new era in dyestuff chemistry commenced and in less than eighty years thousands of new dyes were synthesised from coal-tar and hundreds of them have found useful application in other industries, such as textiles, leather, paper, paints, ink, etc. The dye industry is intimately connected with the manufacture of explosives, as the primary and intermediate products are the same in the two cases. It is thus a "key industry" and this fact brought home vividly to the British Government during the First World War (1914-18) when the supplies of these products were cut off. In 1913, Germany produced coal-tar dyes of the value of about £20,000,000 representing about three-fourths of the world's production. Although the coal-tar dye industry originated in England with the discovery of Perkin, it did not flourish in that country. The causes of its failure in England were two : firstly, the neglect of organic chemistry in the universities prior to 1880 by which time a part of the business of manufacturing colours from coal-tar had already passed into the very competent hands of the Germans ; and, secondly, the British manufacturers' disregard of the application of scientific and research methods to industrial processes.

Similarly, Sabatier's discovery that unsaturated organic compounds which are ordinarily indifferent to gaseous hydrogen could be successfully made to take up hydrogen with the aid of certain catalysts has had a far-reaching effect in the technical practice known as the "hardening of fats and oils."

Although we are as yet far from synthesising proteins, starches and celluloses, organic chemistry has been widely applied in the different industries. The textiles, artificial silks, paper making, films, plastics etc., require the help of the chemist. The "process and product control" enables the manufacturer to turn out a uniform and high quality product.

Natural petroleum, which is a complex mixture of hydrocarbons, had been known from very early times, and the "eternal fires of Baku" were known to fire-worshippers as early as 600 B.C. The economic exploitation and development of the petroleum industry, however, commenced after Kekule had placed organic chemistry on a scientific basis in 1858. When these natural resources are exhausted as they must certainly be, in a few decades, services of organic chemistry will be required in producing cheap power alcohol or some other substitute for motive power. The enumeration of the services which organic chemistry has rendered or will render in future to industry is not exhausted, but enough has been said to show its tremendousvalue.

PART I

ORGANIC ANALYSIS AND GENERAL THEORY

CHAPTER ONE

METHODS OF PURIFICATION AND CRITERIA OF PURITY

1. Purification of Organic Substances.—Most of the organic substances when first prepared are impure. Before they can be systematically investigated, it is necessary that they should be obtained in a pure state. The various methods employed for this purpose are given below.

2. Crystallisation.—The method of purifying an organic substance by crystallization is essentially the same as that employed for inorganic compounds, except that solvents such as alcohol, ether, light petroleum, chloroform, benzene, etc., are employed in addition to water. A hot, nearly saturated solution of the substance in a suitable solvent is first prepared. Any insoluble matter that may be present is filtered off, and the clear, hot solution allowed to cool; crystals of the substance separate out, while the impurities are left behind in the mother liquor. The details of the procedure are—

(1) **Preparation of solution.** The first thing to do in this connection is the selection of the right solvent. Small amounts (a few milligrams will suffice) of the substance are put into a number of small test tubes, and treated with a small quantity of each of the common solvents. If the substance dissolves immediately in the cold, or if practically no dissolution occurs on warming, the solvent under trial is unsuitable, The suitable solvent will be that in which the substance dissolves on heating and from which it readily crystallizes out on cooling.

Having made a selection of the solvent, we must next determine the amount of it to be used. It should be just sufficient to make the solution, when hot, nearly saturated. Too large an excess of the solvent should be avoided, otherwise no crystals will form on cooling. It should be remembered that the substance to be purified often contains insoluble impurities, and no attempt must be made to bring these into solution by the addition of a large amount of the solvent.

A suitable quantity of the well-powdered substance along with the necessary amount of the solvent, is placed in a flask. If dissolution occurs readily, the

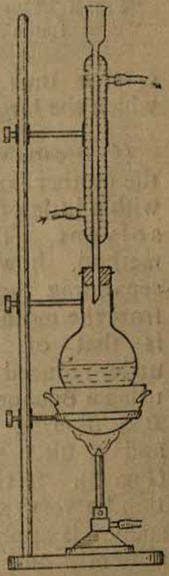

Fig. 1.

flask is gently warmed on a water bath. Should it, however, be too slow, the flask is fitted with a reflux condenser and heated on the water- or sand-bath (Fig. 1). This arrangement prevents the loss of the solvent by evaporation during the process of solution, and also protects the vapour of the solvent, if inflammable, from catching fire.

(2) **Filtering the hot solution.** If the quantity of the solution is small, it may be filtered through an ordinary filter paper placed in a glass funnel with a short stem or a fluted filter fitted in a fluted funnel. In either case, the funnel must be warmed just before filtering.

In case the amount of the solution is large, the glass funnel containing the filter paper is placed in a hot-water funnel (Fig. 2). This consists of a double-walled copper funnel provided with a side-tube, *S*, for heating. It must be remembered in this connection that if the vapour of the solvent is inflammable, the flame *must* be put out before starting the actual filtration.

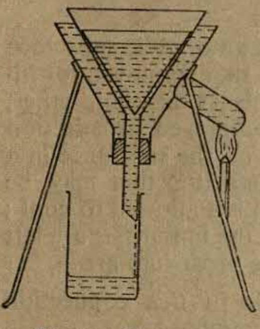

Fig. 2. Hot water funnel.

(3) **Crystallizing.** The hot filtrate is allowed to cool as slowly as possible in a beaker covered with a watch-glass, with the convex side upwards. In this manner, large beautiful crystals are obtained. For analytical work, however, small-sized, pure crystals are required. These are readily obtained by cooling the hot solution rapidly, say, by placing the beaker in cold water. The crystals thus obtained are free from droplets of the mother liquor, which the larger crystals are very liable to occlude.

(4) **Separating crystals from mother liquor.** If the crystals are large, the mother liquor can be readily poured off and the crystals washed with a little of the pure solvent. The best method, however, of separating the crystals from the mother liquor is that of filtration under reduced pressure using a Buchner funnel, *B*, a filtering flask, *F*, and a filter pump, *P* (Fig. 3). If the filtration be very slow, the suction is applied intermittently and a filtering flask, *F*, provided with a stop-cock, is used. When the pump

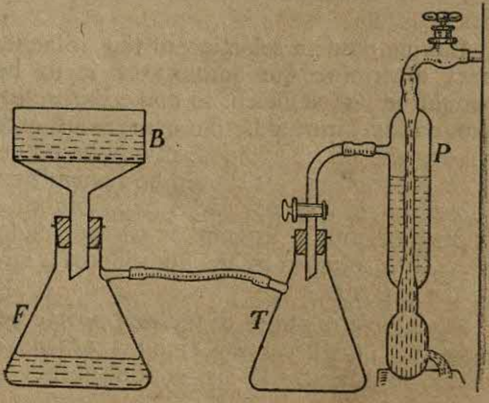

Fig. 3. Filtration under reduced pressure.

has been working for some time, the stop-cock is closed, and the pump disconnected. A tube, closed at the upper end and open at the lower, may be placed inside the filtering flask. This serves as a vacuum-gauge. So long as the vacuum inside the filtering flask is perfect, the level of the liquid inside and outside the tube will be the same ; but if air enters the flask, the liquid will rise into the tube, thus indicating a leakage. The trap, *T*, prevents the liquid left in the body of the pump, *P*, from being sucked into the filtering flask, *F*.

For handling large amounts of material in technical operations, a centrifugal machine is most frequently used.

Fig. 4 shows a centrifugal machine for drying crystals, designed by Professor Richards of Harvard University. It is specially suitable for chemical and sugar laboratories. The crystals to be dried are put into the perforated drum, *D*, made in this case of porcelain. The outer bucket *B*, is also of porcelain and is provided with a draining nozzle, *N*. The drum is made to rotate at a speed of about 1,000 revolutions per minute, by means of the electric motor, *M*. The dry crystals are left inside the drum, while the mother liquor, which previously adhered to the crystals, passes out through the perforations into the outer bucket.

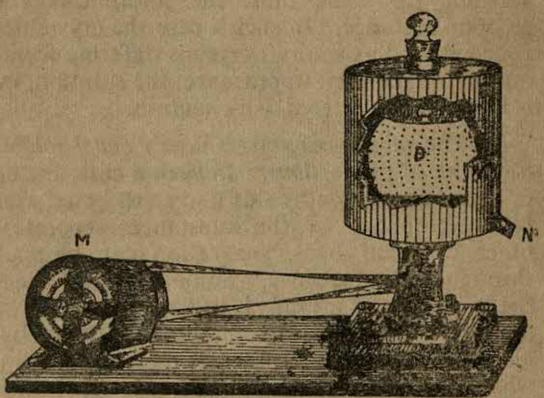

Fig. 4. Centrifugal Machine.

3. Fractional Crystallization.—The method of simple crystallization is only suitable for the purification of a single substance, contaminated with *small* quantities of impurities. When it is desired to separate two (or more) substances, both of which are soluble in the solvent used, the method of *fractional crystallization* must be employed. Three different cases arise :—

(1) *The substances differ considerably in their solubilities.* In such a case it is usually easy to find a solvent which will dissolve a large portion of the more readily soluble constituent and but a little of the less soluble. If we treat the mixture with a suitable quantity of the solvent, we will get a solution that contains practically the whole of the readily soluble constituent, *B*. The solution is filtered from the residual solid. Thus we are able to resolve the mixture into two fractions : (*a*) the solution, and (*b*) the residue.

The solution is now evaporated to a certain point ; *B* crystallizes out, unaccompanied by any of the *A*. The crystals of *B* are filtered off, and the solution is allowed to evaporate in order to get crystals of *A*.

The crystals of *B* and the residue from the first operation are dissolved in a fresh quantity of the solvent. On evaporating this solution, *B* will crystallize out practically free from *A*.

On repeating the crystallization of the two fractions a second time, we get a practically complete separation of *A* and *B*.

(2) *The substances possess nearly equal solubilities, but the proportion of the one is considerably greater than that of the other.* The separation of such a mixture is also comparatively easy. On cooling the hot solution of the two substances in a suitable solvent, the constituent present in larger quantity crystallizes out first. After standing for some time, the solution may deposit crystals of the second substance. In such a case the crystallization must be carefully watched, and as soon as crystals differing from those that separated out first make their appearance, the solution, even though still warm, is immediately filtered with suction.

(3) *The substances possess nearly equal solubilities and are present in nearly equal proportions.* In such a case, the crystals of the two compounds appear side by side and must be separated mechanically. For instance, if one of the substances separates in big crystals and the other in small ones, separation can be readily effected by sifting through a suitable sieve. Sometimes, difference in specific gravity of the two kinds of crystals is utilized for their separation. A rotatory motion is imparted to the mother liquor by rapidly stirring with a glass rod. The lighter crystals thereby rise to the top of the liquid, while the heavier ones collect at the bottom of the vessel. The mother liquor with the lighter crystals floating in it is rapidly poured off. As a last resort, the two compounds may be separated by picking out the individual crystals by hand.

4. Sublimation.—Certain substances are converted by heat into vapours, which, when condensed on a cold surface, do not pass into

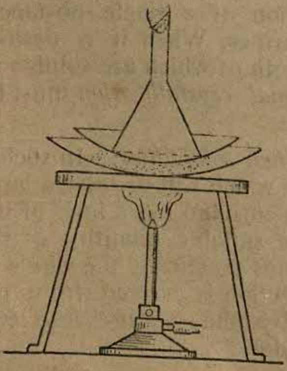

Fig. 5. A simple sublimation apparatus.

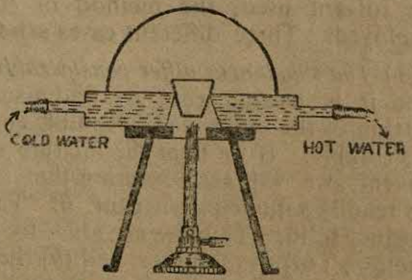

Fig. 6. Bruhl's sublimation apparatus.

the liquid state, but deposit directly in the form of crystals. The process is known as sublimation. Some of the substances which can be readily purified by this process are:

Naphthalene,	Camphor,
Anthracene,	Benzoic Acid.

A simple method of sublimation consists in placing the substance to be sublimed on a watch glass heated very slowly on a sand-bath with a free flame. The watch-glass is covered with an inverted funnel, somewhat smaller than itself (Fig. 5). Over the edge of the funnel is stretched a perforated filter paper. This prevents the small, light crystals of the substance from falling back on to the watch-glass. The upper surface of the funnel may be kept cool by covering it with layers of wet filter paper.

A very efficient apparatus for sublimation is that designed by Bruhl (Fig. 6). This consists of a hollow, metallic vessel provided with inlet and outlet tubes for circulating water, and having in the middle an opening of the shape of an inverted, truncated cone. The substance to be sublimed is placed in a crucible supported in the opening as shown in the figure, and the whole is covered with a glass dish. The substance sublimes, in part on the inside of the glass dish, but more abundantly on the upper, cold surface of the metallic vessel.

Sublimation in Air. An efficient device for carrying out sublimation at a comparatively low temperature consists in doing so in a current of air or an inert gas (*e.g.*, N_2 or CO_2). A simple form of the apparatus is shown in Fig. 7. The substance to be purified is placed in a conical flask, *F*, fitted with a double bored cork carrying (*i*) an inlet tube for air and an adapter. The latter fits loosely into the mouth of a round-bottom flask, *R*, acting as the receiver. A plug of glass wool serves to keep the connection safe for the outlet of air. The flask *F* is heated, when the substance sublimes out of it in the pure state, and collects on the inside of *R*. A stream of cold water keeps the receiver cool.

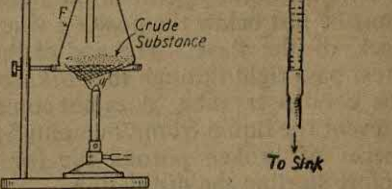

Fig. 7. Sublimation in air.

5. **Distillation.**—Distillation is the process of converting a liquid or solid into a vapour, which is then condensed. When a solid is distilled, we do not get the crystals directly as is the case in sublimation. The distillate is a liquid which may subsequently solidify into a crystalline mass. The process of distillation is used for freeing a volatile substance from non-volatile impurities, or from substances

which are far more, or far less, readily volatile than the substance to be purified.

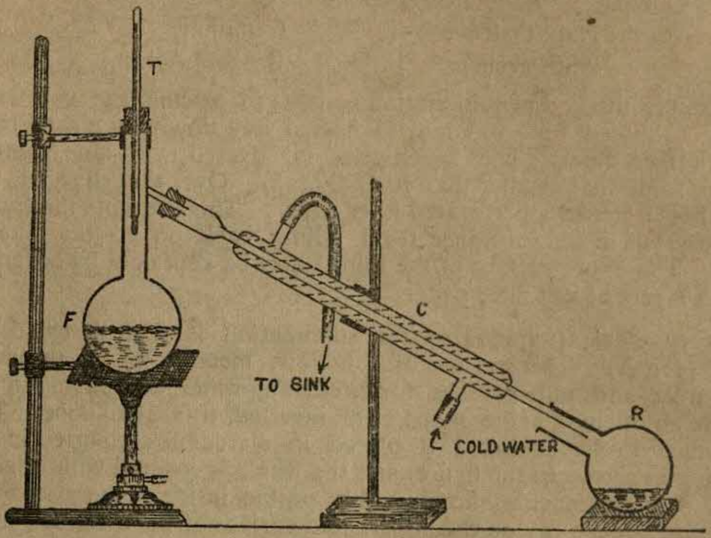

Fig. 8. Distillation apparatus.

The usual form of apparatus employed in distillation is shown in Fig. 8. It consists of—

(1) *a distillation flask, F,* provided with a side-tube,

(2) *a Liebig condenser, C,* and

(3) *a receiver, R.*

A thermometer, *T*, is usually fitted into the neck of the flask in order to note the boiling-point of the liquid. The bulb of the thermometer must be just below the position where the side-tube is fused into the neck of the flask. The end of the side-tube of the distillation flask must pass right through the cork, so that the distillate, as it falls into the condenser tube, does not come into contact with the cork. To prevent the liquid from "bumping" (sudden violent ebullition), a few pieces of broken porous tile (or some glass beads) are added to it before starting the distillation.

In case the object is not to determine the boiling point, but to distil a fairly large quantity of the liquid, the thermometer may be replaced by a dropping funnel. From this the liquid to be distilled is made to drop continuously at the same rate as that at which the distillate passes.

When the boiling-point of the liquid lies above 170°C, there is great danger of the condenser tube getting cracked. In such a case, therefore, a straight glass-tube, called an **air-condenser**, is used instead of the water-cooled condenser.

6. Fractional Distillation.—This process is employed for separating a mixture of two or more miscible liquids, the boiling points of which are sufficiently removed from one another. The method is similar to ordinary distillation, except that portions of the distillate passing at different temperatures are collected separately. The boiling must be made to proceed slowly and evenly, so that it may be possible to count the individual drops as they fall into the receiver.

On distilling a mixture of two liquids, say benzene (*b. p.* 80°) and toluene (*b. p.* 111°), more of the lower boiling liquid passes over at the beginning and more of the higher boiling one at the end, of the operation, the composition of the distillate changing continuously. In order to effect a separation of benzene-toulene mixture, the distillate may be best collected in 5 fractions ; *A* from 80° to 85° ; *B* from 85° to 91° ; *C* from 91° to 98° ; *D* from 98° to 105° ; *E* from 105° to 111°. The different fractions are collected in labelled flasks, and their respective volumes noted. The portion of the liquid which does not distil up to 111° is rejected.

The process of distillation is now repeated as follows : The contents of flask *A* are transferred to the distillation flask and redistilled, the distillate passing at 80° to 85° being collected in the same flask, *A*. When the temperature reaches 85°, the distillation is stopped and the contents of flask *B* added to the distillation flask. The distillation is continued once again, and the fraction passing at 80° to 85° is collected in flask *A* and from 85° to 91° in the flask *B*. As soon as the temperature reaches 91°, the distillation is again stopped and the contents of flask *C* added. The distillation is once more continued and the fractions passing at 80° to 85°, 85° to 91° and 91° to 98° are collected in flasks *A*, *B* and *C* respectively. The process is carried on in the above manner, until all the fractions have been added.

The five fractions collected during the second distillation are submitted to the same process as before and the operation repeated a number of times. Each time the fractionation is repeated, the volumes of the fractions *A* and *E* increase while those of fractions *B*, *C* and *D* continuously decrease. When the total amount of the liquid in flasks *B*, *C* and *D* becomes very small (say less than one-tenth of the total amount of the liquid) the refractionation may be stopped.

The process of fractional distillation may be carried out in a fractionating flask, *i.e.*, a distillation flask with a sufficiently long neck. If large quantities of a mixture are to be handled, an ordinary round-bottom flask of a suitable capacity can be converted into a fractionating flask by using a fractional-distillation tube, as shown is Fig. 9. The process of fractionation, however, is rendered more efficient and rapid by using a fractionating column (Fig. 10) connected to the neck of the boiling flask. The

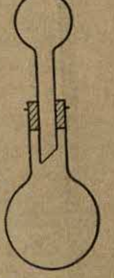

Fig. 9. Round bottom flask fitted with fractional-distillation tube and thermometer.

fractionating column aids the separation by working in the opposite way to the boiling process. As the vapour passes upwards through the column, it gets partially condensed by the cooling action of the air. The condensate flows down the column, and forms a layer around each disc, glass-bead, or ring contained in the column. In this manner, the upgoing vapour is brought into a continuous contact with the down-flowing liquid, whereby the vapour is thoroughly scrubbed. The scrubbing aids the separation both by partial evaporation of the liquid and partial condensation of the vapour; there occurs a continuous exchange of constituents between the vapour and the liquid. Thus, by the time the vapour

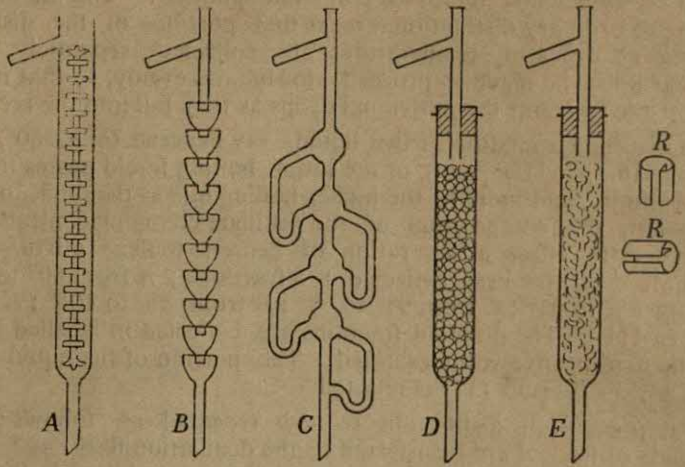

Fig. 10. Different types of fractionating columns; (*A*) Young's rod-and-disc type; (*B*) Young's pear-shaped type; (*C*) Le Bel-Henninger column; (*D*) Hempel's column filled with glass beads; (*E*) Still-head filled with Lessing's contact rings *R*, *R* (shown on a large scale on the right of *E*).

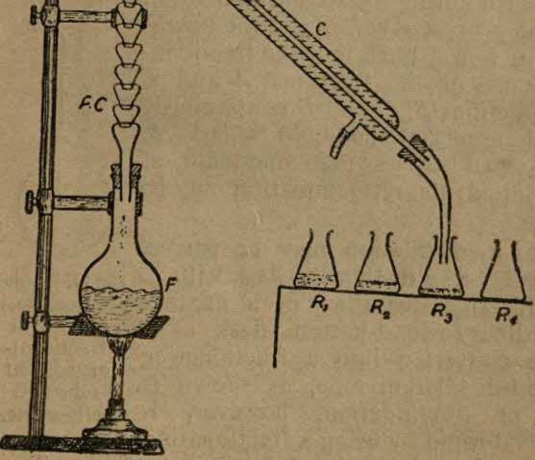

Fig. 11. Fractional distillation.

reaches the top of the column, most of the less volatile constituent has been condensed. Similarly, the more volatile constituent contained in the down-flowing liquid will be completely removed by the time the latter flows down into the distillation flask. In this manner a more thorough separation of the constituents is effected than is possible with an ordinary long necked distillation flask. The use of a fractionating column renders the number of distillations much smaller, though, as a rule, it cannot entirely do away with the necessity of redistilling.

The various types of fractionating columns used in the laboratory are shown in Fig 10 ; of these, the most efficient is the one packed with Lessing's contact rings.

The apparatus used in fractional distillation on the laboratory scale is shown in Fig. 11. The mixture is distilled from a round-bottom flask, *F*, fitted with a fractionating column, *FC*. The latter is provided with a thermometer, *T*, and is connected to a water-cooled condenser, *C*. The successive fractions of the distillate are collected in the receivers R_1, R_2, R_3 and R_4.

7. Industrial Fractionation.—For the separation of mixtures of volatile liquids on a commercial scale, very carefully designed fractionating columns are used which may attain a height of 30 feet or more. The *Coffey Still*, used for rectifying aqueous alcohol, the long air-cooled vertical columns, employed for the separation of the crude petroleum into various fractions, and the plants employed for the fractionation of 90 per cent and 50 per cent benzol, to obtain pure benzene, toluene and xylene, are important examples of the use of fractionating columns in chemical industries.

Fig. 12 shows the bell-and-plate fractionating column, frequently used in industrial fractionation. The mixed vapour from the still, *S*, enters compartment 1 of the fractionating column, as shown by arrows in the figure. Here it gets partially condensed, and the condensate, consisting of the higher boiling constituents, collects on the plate. An overflow pipe allows the condensate to flow back into the still. The more volatile components pass on to compartment 2, and so on. In this manner, the lower-boiling components get separated from the higher-boiling ones. The former may be led off from the top of the column and the latter withdrawn from the bottom.

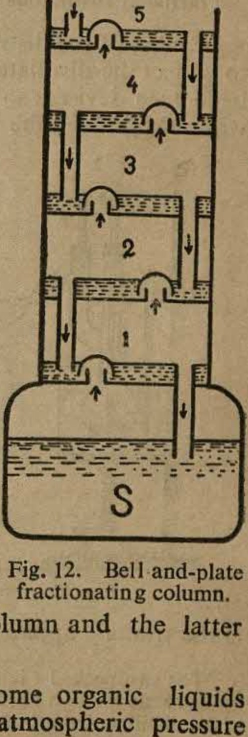

Fig. 12. Bell-and-plate fractionating column.

8. Distillation under Reduced Pressure.—Some organic liquids which decompose at their boiling points under atmospheric pressure may be distilled without decomposition under low pressure. Thus glycerine boils with partial decomposition at 290° under 760 mm. pressure. It may be distilled without decomposition at 180° under a reduced pressure of 12 mm.

The usual form of apparatus used in vacuum distillation is shown in Fig. 13. The liquid to be distilled is placed in a two-necked distillation flask[1] *F*. Through one of the necks passes a thermometer, *T*, and through the other a capillary tube, *C*, which is drawn out at its lower end to a capillary dipping into the liquid and is almost closed at its upper end by means of a piece of rubber tubing and a screw clamp. This arrangement prevents bumping, which is more pronounced during vacuum distillation than during distillation under ordinary pressure. The evacuation of the apparatus is effected by means of a water or mercury pump. In the former case, the lowest pressure obtainable is that of aqueous vapour at the room temperature (*i.e.*, usually 10 to 25 mm.). With a mercury pump, pressures lower than 1 mm. can be readily obtained. A manometer, *M*, is introduced between the receiver and the pump to ascertain the pressure under which the distillation takes place. All corks must be made perfectly air-tight by coating them with collodion after the apparatus has been fitted up.

Fractional Distillation under Reduced Pressure.—

In most of the distillations under reduced pressure it is necessary to collect the distillate in fractions. Many ingenious forms of receiver have been devised, so as to allow the collection of various fractions without breaking the vacuum. The best known of these arrangements is the triangle apparatus shown in Fig. 13. When it is desired to

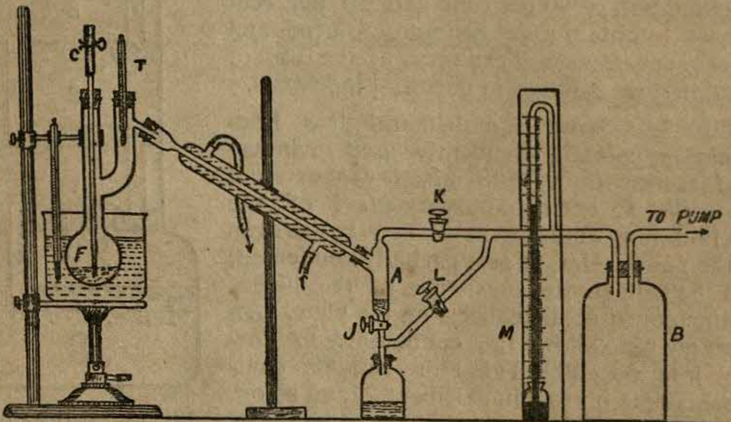

Fig. 13. Fractional distillation under reduced pressure.

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[1] The two-necked Claisen flask is to be preferred in distillation under reduced pressure as the two necks greatly reduce the danger of mechanical contamination of the distillate from bumping or frothing.

change the receiver, the cock *J* is turned off, *K* is turned on, while the three-way cock, *L*, is turned so that the receiver is put in communication with the outside air and not with the pump ; meanwhile the distillate goes on collecting in *A*. The receiver is now changed, the cock *L* is turned so that the receiver is once again put into communication with the pump. After a short time, the cock *K* is closed and *J* opened, so that the distillate in *A* flows down into the new receiver.

9. **Steam Distillation.**—The process of steam distillation is employed for separating those substances which are appreciably volatile at 100° from non-volatile components of a mixture. The apparatus employed is shown in Fig. 14. The mixture to be treated is placed, along with some water, in a large-size round-bottom flask, *F*, heated on a sand-bath and connected to a condenser, *C*. The flask is held in a sloping position, so that during the vigorous ebullition which occurs, none of the mixture may be thrown up into the tube leading to the condenser. Steam from the boiler *B* (which generally consists of a tin can, provided with a safety tube, *S*), is rapidly passed through the liquid in the flask *F*. The heating of *B* and *F* are controlled, so as to keep the quantity of the liquid in *F* constant. In the case of an oily liquid, or a solid substance, the distillation should be continued for about 15 minutes after drops of oil, or particles of solid, have ceased to appear in the condenser. In the case of a soluble acid, the distillation should be stopped when the distillate no longer gives an acid reaction with litmus.

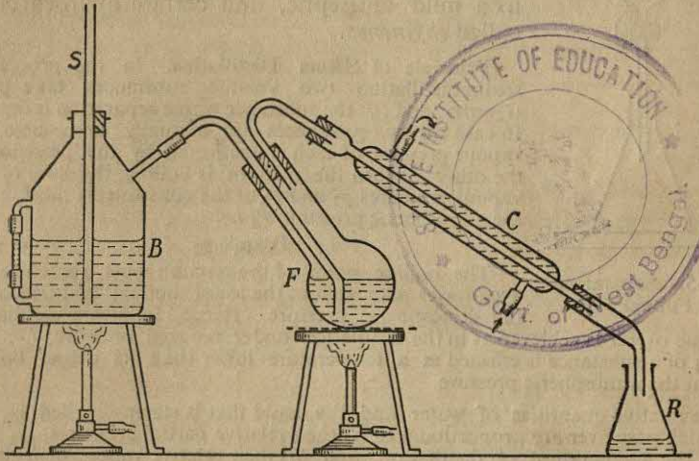

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Fig. 14. Apparatus for Steam Distillation.

The distillate in the receiver consists of water and the substance whose separation is desired. In case the substance is an oily liquid, it is separated from the water by means of a separating funnel

(Fig. 15) ; if it is an insoluble solid, it is separated by filtration. If the substance is a soluble acid, the liquid is exactly neutralized with sodium carbonate, and the solution evaporated to dryness. From the pure sodium salt, thus obtained, the acid may be recovered by distilling with sulphuric acid. The substances usually purified and separated by the process of steam distillation are aniline, bromobenzene, *p*-dibromobenzene, essential oils, petroleum, turpentine oil etc.

The *ajwain* oil, on fractional distillation, gives *thymol*, a colourless crystalline substance, used as a mild antiseptic, and certain hydrocarbons, called *thymenes*.

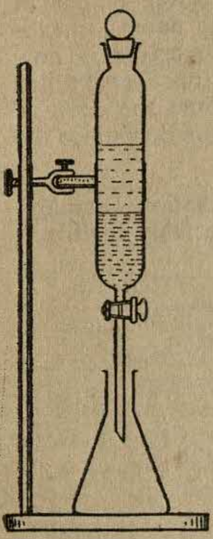

Fig. 15. Separating Funnel.

Principle of Steam Distillation. In the process of steam-distillation two volatile substances take part: (*i*) water, and (*ii*) the substance whose separation is desired. In case the two substances are mutually immiscible, the vapour pressure of each is unaffected by the presence of the other. When the mixture is boiling, the sum of the vapour pressures p_1 and p_2 of the constituents must equal the atmospheric pressure, *P*, *i.e.*

$$P = p_1 + p_2.$$

The boiling point of the mixture must, therefore, be even lower than that of the lower boiling constituent at the atmospheric pressure. Hence, in steam distillation the same object is achieved as in the distillation under reduced pressure, *i.e.*, the boiling of a substance is effected at a temperature lower than its actual boiling point at the atmospheric pressure.

The relative quantities of water and the liquid that is steam-distilled, w_1 and w_2, which pass over are proportional to (*i*) their relative partial pressures, p_1 and p_2 at the temperature of distillation, and (*ii*) their relative vapour densities or molecular weights. Now, the molecular weight of water is 18. If *M* is the molecular weight of the substance that is being steam-distilled, we have:

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

Example. *What weight of aniline, $C_6H_5NH_2$, will be carried over by 100 gm. of steam at 99·4°C, the atmospheric pressure being 760 mm.? The aqueous tension at 99·4°C is 747 mm.*

Molecular weight, *M*, of aniline, $C_6H_5NH_2 = 72+5+14+2 = 93$

Partial pressure, p_1, of steam $= 747$ mm.

Partial pressure, p_2, of aniline $= 760 - 747$ mm. $= 13$ mm.

Weight of aniline, w_2, carried over by 100 gm. of steam at 99·4°C.

$$= 100 \times \frac{p_2 \times M}{p_1 \times 18}$$

$$= 100 \times \frac{13 \times 93}{747 \times 18} = \mathbf{8{\cdot}99\ gm.}$$

10. Dialysis.—This process is employed for the separation of crystalloids from colloids. The mixture is placed in a *dialyser*, an apparatus consisting of a shallow glass cylinder over the lower end of which is stretched a parchment paper or a piece of muslin impregnated with collodion (Fig. 16). The dialyser is made to float in a trough of pure water, which is changed from time to time. The crystalloid molecules diffuse out through the parchment paper, while the colloid remains behind in the dialyser.

The "diffusion process" for the manufacture of cane-sugar from beets and the recovery of cane-sugar from molasses are examples of the application of dialysis in technical organic chemistry.

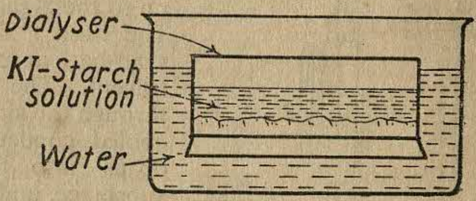

Fig. 16. Dialyser.

11. Extraction with Solvents.—The process of extraction with solvents is employed in the following three cases :—

(1) *Isolation of a Substance Dissolved or Suspended in a Liquid* (usually Water). The separation of the substance is effected by agitating the liquid with a solvent in which the substance is more readily soluble but which is not miscible with the first liquid, drawing off the solution of the substance in the new solvent, and distilling off the latter. The most commonly used solvent for this purpose is ether, though, in certain cases, carbon disulphide, petroleum ether, chloroform and benzene, are also used.

A familiar example of ether extraction is that of aniline. This substance is prepared by the reduction of nitrobenzene, and is separated from the reaction mixture by steam distillation. The distillate separates into two layers : a lower layer of aniline, and an upper layer consisting of an aqueous solution of aniline, which also contains a quantity of aniline in the form of minute droplets that do not settle quickly (*i.e.*, emulsion). The lower layer can be separated by means of a separating funnel, and presents no difficulty. To recover aniline from the aqueous layer, it is shaken up with ether, in which aniline is much more soluble than in water, and the upper ethereal solution of aniline is separated from the lower aqueous layer by means of a separating funnel. The lower aqueous layer is once again shaken up with a little more of ether, and the ethereal layer again separated. Finally, aniline is recovered by boiling off the ether.

(2) *Isolation of a Substance from a Solid Material.* The more important examples of extraction of this type are : the extraction of alkaloids from leaves and bark of plants, of flavouring extracts from seeds, and of oils from crushed seeds and oil cake.

The **Soxhlet Extractor** (Fig. 17), which is frequently used in chemical laboratories for the extraction and estimation of a fat or oil in a material, *e.g.*, oil seeds and oil cake, is a very convenient apparatus for this purpose. The powdered material is put into a *thimble T*, made of stout filter paper and placed inside the glass tube, *G*. The latter is provided with a syphon, *S*, and a side-tube, *S.T*. The length of the thimble should be such that it extends about 1 cm. above the highest point of the syphon tube. The amount of solvent taken in the boiling flask *F* should be $1\frac{1}{2}$ to 2 times the volume of *G* up to the highest point of the syphon. The flask *F* is heated on a water-bath or sand-bath according to the nature of the solvent. The vapour of the solvent rises through the side-tube up into the water-cooled condenser, *C*. The condensate drops into the thimble, dissolves the substance, and filters out into the space between the thimble and the glass tube. As soon as the liquid level in *G* reaches the highest point of the syphon, the solution automatically flows back into the boiling flask. The process may be continued for as long a time as necessary. At the end of the operation, the solvent is boiled off, and the isolated substence weighed, if necessary.

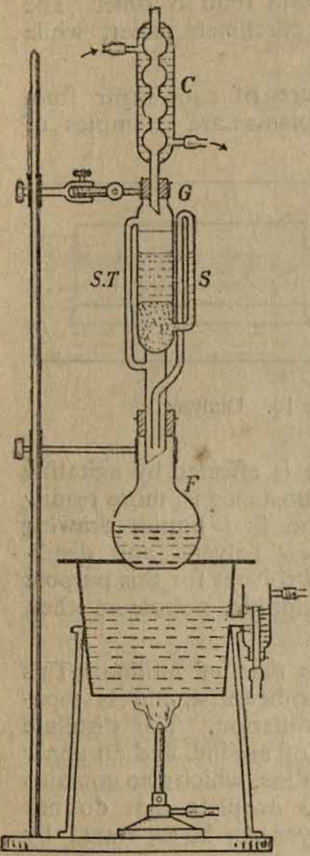

Fig. 17. Soxhlet Extractor.

(3) *Removal of Soluble Impurities from Mixtures*. This is of great importance in the purification of organic substances. The principle involved is similar to (2), except that the solvent extracts the impurities, leaving behind the desired substance in a more or less pure condition. Here, as in (2), several extractions with small portions are more effective than a single extraction with the whole of the given quantity of the solvent.

Distribution Law. The process of extraction with solvents is based on the distribution law or *partition law*. If we shake up a substance with two immiscible solvents, say succinic acid with ether and water, it will distribute itself between the two solvents in such a manner that a definite ratio is maintained between the two concentrations, *i.e.*,

$$\frac{\text{Concentration of solute in ether}}{\text{Concentration of solute in water}}=K$$

This ratio is called the *partition coefficient* of the substance for the two solvents. Its value for the distribution of succinic acid between water and ether at 15°C is 5·4. It can be readily shown that a given amount of a solvent will effect a more complete extraction when used in several small portions than when used in one lot.

12. Chromatography.[1] The technique known as *chromato-*

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[1] Early experiments on this subject were made with substances having different colours, resulting in a series of coloured bands at the end of the separation; hence the term "*chromatography*".

graphy, or **partition chromatography**, is a special case of solvent extraction in which a suitable adsorbent material is employed instead of a liquid solvent. It is based on the fact that different constituents of a mixture present in a solution are adsorbed to different extents by a given adsorbent (**Selective Adsorption**) If a solution containing a number of solutes. is poured down a **long column packed with an adsorbent** having sufficiently different adsorptive power for the components present in a solution, the material taken up by the upper layer of the adsorbent will consist largely of the solute that is most readily adsorbed together withe smaller proportions of the rest. These latter will be gradually adsorbed as the solution passes further down the column of the adsorbent material. The partial separation of the components, thus effected, is completed further by **allowing a small quantity of the pure solvent to flow slowly down the column.** The less readily adsorbed constituents are thus dissolved out from the upper layer (**Selective Desorption**) and readsorbed lower down. In this way, the adsorption of each component gets distributed in different layers of the adsorbent, the most strongly adsorbed component being, of course, in the topmost and the least readily adsorbed component in the lowermost layer (Fig. 18). • At the end of the operation, the column of the adsorbent is pushed out of the tube and cut up into sections from which different components can be extracted. In case the components are **coloured**, as they were in earliest experiments, the separate layers of the adsorbent column can be readily seen. In other cases, use may be made of **ultra-violet light** in which the components exhibit different fluorescent behaviour.

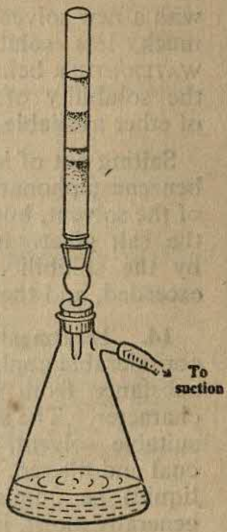

Fig. 18. Chromatography.
The vertical glass tube is packed with a suitable adsorbent (say cellulose pulp). The solution containing the substances is sucked up through the tube. The passage-down of the solution is facilitated by using a suction-pump.

Selective adsorption is also employed for the **industrial recovery of volatile solvents.** Their very dilute vapours are adsorbed from the air by active carbon or silica gel. The separation of adsorbable gases or vapours may also be carried out from a flowing system, the gases being passed through pipes containing a suitable adsorption material.

13. Salting Out.—Many organic substances which are soluble in pure water are insoluble or sparingly soluble in aqueous solutions of certain salts, notably sodium chloride, potassium carbonate, calcium chloride, and Glauber's salt. Hence, when a solid salt is added to an aqueous solution of an organic substance, *e.g.*, ethyl alcohol, acetone, aniline, pyridine, etc., the substance is thrown out of solution and may be separated by means of a tap funnel or preferably by extraction with ether.

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A combination of salting-out and ether-extraction has many advantages. The addition of the salt to the aqueous solution before extraction with ether helps the extraction (*i*) by partially throwing the dissolved substance out of solution, (*ii*) by exchanging water with a new solvent, *viz.*, the salt solution, in which the substance is much less soluble than in pure water, the partition coefficient, WATER/ETHER being thereby greatly reduced, and (*iii*) by lowering the solubility of ether in water, and thus making a larger proportion of ether available for extraction.

Salting out of ionized organic substances, *e.g.*, soap and sodium benzenesulphonate, by common salt is due not only to the change of the solvent, but also to the *common-ion effect*. The addition of the salt greatly increases the concentration of the sodium ion, whereby the solubility product of sodium benzenesulphonate, etc., is exceeded, and the substance is, therefore, thrown out of solution.

14. Treatment with Animal Charcoal.—Animal charcoal finds considerable application in organic chemistry to free a colourless substance from coloured impurities, and also impurities of a tarry character. The substance in the liquid state, or in solution with a suitable solvent, is boiled with the requisite amount of animal charcoal and filtered. If the solvent used (or the substance itself, if liquid) be immiscible with water, the animal charcoal, which is generally moist, is dried on a water-bath before use.

In some petroleum refineries a specially prepared paddy-husk charcoal is used for decolorizing lubricating oils and melted paraffin wax. Another very efficient substitute for animal charcoal, which is much used for refining sugar in Germany, is a mixture of fine wood-meal and floated infusorial earth (*kieselguhr*). Its decolorizing power is said to be far greater than that of animal charcoal.

15. Drying of Organic Substances.—No organic substance can be regarded as pure, if it contains even traces of moisture. The drying of starting materials and of finished preparation, therefore, is an important feature of organic practical work.

Solid substances are dried in a number of ways. If sufficiently stable, they may be dried in a steam or air-oven or by heating on a free flame. If unstable on heating, the substance is allowed to stand in the air, or, better still, in a vacuum desiccator (Fig. 19) containing a suitable drying agent.

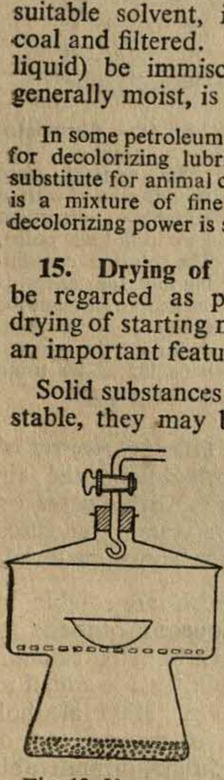


Fig. 19. Vacuum Desiccator.

Before a solid substance is finally dried as given above, the adhering moisture must be removed (*i*) by pressing it between folds of filter paper, (*ii*) by pressing it on an unglazed porcelain plate, or (*iii*) by means of a centrifuge (Fig. 4.).

Organic liquids, or solutions of organic solids and liquids in suitable solvents, are dried by letting the liquid stand in contact with a suitable drying agent. The drying agent employed in a particular case must satisfy the following conditions :

(1) It must be practically insoluble in and chemically indifferent towards the liquid to be dried.

(2) It must remove water efficiently.

A list of suitable desiccating agents for different classes of organic substances is given below :

Substance	Desiccating Agents
1. Hydrocarbons and Ethers.	Anhydrous calcium chloride, metallic sodium, phosphorus pentoxide.
2. Alcohols.	Quicklime, anhydrous potassium carbonate, anhydrous magnesium sulphate or sodium sulphate.
3. Haloid Derivatives.	Anhydrous calcium chloride, anhydrous magnesium sulphate or sodium sulphate.
4. Aldehydes and Ketones.	Anhydrous magnesium sulphate or sodium sulphate, anhydrous calcium chloride.
5. Organic Acids.	Anhydrous magnesium sulphate or sodium sulphate, phosphorus pentoxide.
6. Organic Bases.	Solid potassium hydroxide, quicklime or soda-lime.

As a rule, *the spent drying agent is separated before distilling off the dried liquid.* If this point is not attended to, the hydrate of the salt produced during desiccation may be dissociated on heating, and hence the liquid passing over remains moist. In the case of metallic sodium, phosphorus pentoxide and quicklime, the removal of the desiccating agent before distillation of the liquid is unnecessary, as the drying agent undergoes a chemical reaction with water to produce a stable, non-volatile product.

A very easy and efficient method of drying organic liquids and solutions of organic substances in suitable solvents is based on the principle of steam-distillation. Thus, when moist aniline is distilled, at first a few drops of a turbid liquid, consisting of a mixture of aniline and water, pass over ; and then follows a clear distillate consisting of pure dry aniline. Again, when a solution of a moist organic substance in benzene is distilled, the first few drops consist of a mixture of benzene and water, the mixture distilling at a temperature lower than the boiling point of pure benzene (80°C). After this, the benzene itself passes over, and the pure dry organic substance is left as a residue.

16. Chemical Methods of Purification.—The physical methods of purifying and separating organic compounds, described in the foregoing sections, are of general application, and are of great value in separating substances that are chemically similar. The chemical methods, on the other hand, are employed in cases of mixtures of substances that are chemically different. The purification of petroleum products and the separation of basic and acidic components of coal-tar are well-known examples, concentrated sulphuric acid and caustic soda solution being employed in both cases. Of the numerous other cases of chemical purification and separation of organic substances, the following may be cited as examples :—

(1) Purification of acetylene by passing the gas through an ammoniacal solution of cuprous chloride and decomposing the product (brown precipitate of cuprous acetylide) with hot, dilute hydrochloric acid so as to regenerate acetylene.

(2) Separation of acetic acid from "pyroligneous acid" of the wood-distillation industry, which is based on the conversion of the acid into calcium acetate and decomposition of the latter with concentrated hydrochloric acid.

(3) The preparation of pure methyl alcohol, absolutely free from acetone, is based on the conversion of the alcohol into the crystalline derivative *methyl, oxalate*, which is then decomposed by boiling with a solution of sodium hydroxide.

17. Methods of Testing the Purity of a Substance.—The following are the common methods for testing the purity of an organic substance.

(1) Melting Point. The usual method for testing the purity of a solid organic substance is the determination of its melting point. This may be done in two different ways :

(*i*) If a comparatively large amount of the substance is available, about 20 grams of it are carefully heated in a wide test tube provided with a thermometer and a ring stirrer. When about three-quarters of the substance has melted, the burner is put out, and the liquid well stirred. The thermometer is read every half minute. The temperature at which the mercury column remains stationary for 2 to 3 minutes is taken as the melting-point of the substance.

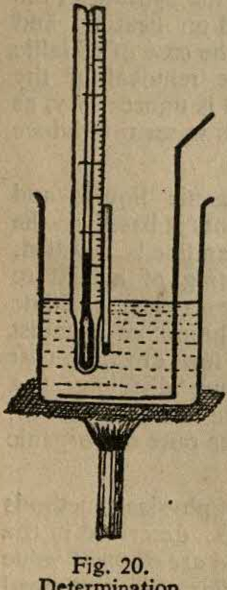


Fig. 20. Determination of Melting Point.

Since the melting-point is defined as the temperature at which the liquid and the solid phases co-exist, it is absolutely necessary that the *solid and the liquefied substance are both present and that the temperature remains constant for a pretty long period.* If the whole of the substance happens to melt, some more of the solid substance must be stirred in, and the lowest constant temperature reached should be noted.

(*ii*) In most cases, however, the quantity of the substance available for the melting-point determination is small. For this reason, the usual method employed in chemical laboratories is as follows : A small quantity of the substance is finely powdered and introduced into a capillary tube, closed at one end. The capillary containing the substance is then moistened with concentrated sulphuric acid, and placed alongside a thermometer, suspended in a beaker containing concentrated sulphuric acid, in such a way that (*a*) the substance in it is at the same level as the middle of the bulb of the thermometer, and (*b*) a little *more than half* of the capillary stands above the surface of the liquid (Fig. 20). This latter arrangement makes the tube cling to the thermometer by capillary attraction.

The acid in the beaker is now heated with a small flame, and constantly stirred with a curved stirrer made of a thin glass rod, the substance and the thermometer being closely watched all the time. The *moment* the substance melts and becomes transparent, the temperature indicated on the thermometer is recorded. The experiment should be repeated, using a *fresh* tube and fresh sample of the substance.

A pure solid has a perfectly definite and sharp melting point. Hence—

(*i*) If the given compound does not melt sharply, it should be taken as impure.

(*ii*) If the identity of the given compound is known, its melting-point is determined experimentally and compared with the true melting-point as given in a book of physical constants. If the two values agree, the given compound may be taken as pure. If, however, the melting-point of the compound is found to be lower, it is evidently impure.

(*iii*) If the identity of the compound is not known, the melting-point of the specimen is first determined. It is then recrystallized from a suitable solvent, and the melting-point determined once again. If there occurs no change in the melting-point, the compound may be taken as pure. But if the second melting-point be higher than the first, the compound is impure.

(2) **Boiling Point.** In order to decide whether a given liquid is pure or impure, its boiling-point is determined by distilling it from a small distillation flask provided with a thermometer. If the liquid is pure, the whole of it would distil at a constant temperature. If, on the other hand, the boiling-point rises during distillation, the liquid is impure.

For a correct boiling-point determination the following points must be carefully attended to :—

(*i*) The bulb of the thermometer should be *wholly* surrounded by the vapour, *i.e.*, no part of it should dip into the liquid.

(*ii*) The vapour should not be allowed to get overheated ; hence the size of the flame should be such that no part of it plays on that portion of the flask which contains the vapour.

(*iii*) The liquid should boil regularly, *i.e.*, without bumping. This is ensured by adding one or two pieces of porous tile to the liquid before starting the distillation.

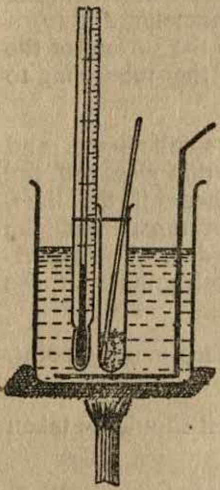


Fig. 21. Siwolowoff's method.

Siwolowoff's Method. The method described above requires a large quantity of the liquid. When only a small amount is available, the following method, due to Siwolowoff, may be used. The apparatus employed in this method is shown in Fig. 21. A few drops of the liquid under examination are placed in the small, thin-walled test-tube attached to the thermometer by means of a rubber band. A capillary tube, sealed about 1 cm. from the lower end, is placed in the test-tube which is then heated in a bath. At first, air bubbles rise from the lower end of the capillary, due to expansion by heat, and these become more and more numerous as the temperature goes up. As soon as a rapid stream of bubbles of the vapour rises through the liquid, the burner is withdrawn from underneath the beaker, and the temperature at which the bubbles *just cease* to come out of the capillary is noted.

QUESTIONS

1. Write an account of the development of organic chemistry into a branch of science, indicating clearly the parts played by Scheele, Berzelius. Liebig, Lavoisier, Wohler, Hennel and Kekule.

2. How would you justify the treatment of organic compounds as a distinct branch of chemistry ? (*Madras, B.Sc., 1941*)

3. What methods are generally employed for the purification of organic compounds ? How can you obtain a sample of pure ether from a mixture of alcohol, acetic acid and ether ? (*Madras, B.Sc., 1943*)

4. What do you understand by *fractional crystallization* and *fractional distillation* ? Give instances of the use of these processes in practical organic chemistry.

5. Describe and explain the process of *steam-distillation* and *distillation under reduced pressure*.

A mixture of nitrobenzene and water boils at 99°C under 760 mm. pressure. At this temperature the vapour pressure of water is 733 mm. What proportion of nitrobenzene will the distillate contain ? (*Ans.* 20.1%)

6. Give an account of the usual methods employed for decolorizing organic substances containing small quantities of coloured impurities.

7. What are the different agents employed in the drying of organic liquids ? Can they be used indiscriminately ? Give illustrative examples to clear your point.

8. Give an account of the methods employed for testing the purity of organic compounds.

9. Describe how you would test the purity of an organic liquid. How would you effect the separation of a mixture of two liquids with boiling-points separated from each other, say by 10°C. (*Punjab, 1930*)

10. Write an account of the various methods by which organic compounds are purified. (*Madras, B.Sc., 1942*)

11. How is purity of organic liquids and solids ascertained ? (*Rajasthan, B.Sc., 1954*)

12. Show how it is possible to separate the following mixture into its pure components, using chemical methods : toluene, phenol and benzoic acid. (*Melbourne, B.Sc., 1954*)

13. Given an organic compound for identification, how would you proceed to determine whether it is a single pure compound, or an impure substance, or a mixture ? (*Banaras, B.Sc., 1958*)

14. Write a short note on chromatic separation. (*Gujarat, B.Sc., 1957*)

15. Draw a sketch of the apparatus used for fractional distillation, using a fractionating column, and explain fully its working. (*Agra, B.Sc., 1958*)

CHAPTER TWO

QUALITATIVE ELEMENTARY ANALYSIS

1. **General.**—Methods of systematic inorganic analysis are based almost entirely on ionic reactions, and consequently, it is always possible to analyse a mixture of two or more inorganic compounds without first separating it into the component substances. In the analysis of an organic substance, on the other hand, we have to depend on reactions that are essentially non-ionic, and liable to be affected considerably by the presence of other substances. For this reason, a mixture of organic substances must always be separated into its components before submitting it to qualitative and quantitative analyses.

The term "qualitative analysis," as used in organic chemistry, usually means the detection of various elements which are present in a given compound. The process, therefore, is often termed **qualitive elementary analysis.** It is a necessary step in assigning a formula to every organic substance.

When the object is to establish the identity of an organic substance, *i.e.*, to prove that it is identical with some compound of known composition and properties, the process is called **identification.** A substance is usually identified by noting its appearance, smell, crystalline form, solubility, elementary composition and reactions, and finally by determining its melting or boiling-point. A very general method of testing the identity of two *solid* substances, *i.e.*, (1) the substance under examination, and (2) the compound with which it is supposed to be identical, consists in mixing a small quantity of each of the two samples and determining the melting-point of the mixture. If this is the same as the melting-point of the individual samples, the identity of the two may be taken to be proved.

If the above methods fail to reveal the identity of the substance under examination, a qualitative elementary analysis, followed, if necessary, by a quantitative analysis, must be made. A complete identification of a compound may, at times, involve the determination of its molecular weight and a study of its chemical reactions.

2. **Elements Occurring in Organic Compounds.**—Besides carbon, the most commonly occurring elements in organic compounds are hydrogen, oxygen, nitrogen, halogens and sulphur ; less common are phosphorus, arsenic and metals.

3. Detection of Carbon and Hydrogen.[1]—The only conclusive test for carbon and hydrogen is as follows : A small quantity of the pure, *dry* substance is mixed with 5 to 10 times its weight of freshly ignited powdered cupric oxide. The mixture is placed in a small, hard glass test-tube and covered with a layer of cupric oxide. The test-tube is provided with a cork carrying a delivery-tube, the end of which is made to dip into some lime-water in another test-tube (Fig. 1). If the substance contains carbon, the latter is oxidized to carbon dioxide, which turns the lime water milky. If it also contains hydrogen, small drops of water will collect in the upper, cool part of the test tube, and may be confirmed with anhydrous cupric sulphate, which changes to blue.

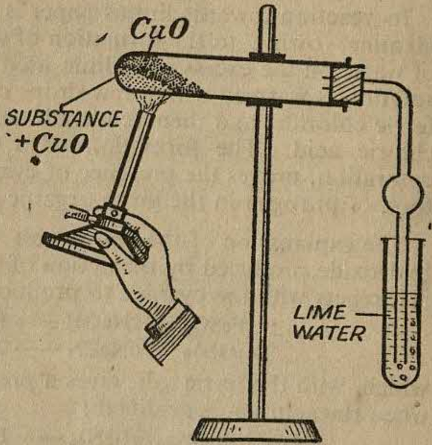


Fig. 1. Testing for carbon and hydrogen.

Expt. 1. By means of the apparatus given in Fig. 1, demonstrate the presence of carbon and hydrogen in urea.

4. Detection of Oxygen.—There is no conclusive qualitative test for oxygen in an organic compound, though its presence may sometimes be inferred indirectly. Thus, if on heating the compound in a dry tube, drops of water condense on the upper, cool portion of the tube, the compound obviously contains oxygen. Again, if the compound has been proved to be a carboxylic acid, alcohol, ether, aldehyde, carbohydrate, etc., it must, of course, contain oxygen.

The only sure way of proving the presence or absence of oxygen in an organic compound is by quantitative analysis. (See Chap. 3, Sec. 4).

5. Detection of Nitrogen.—(1) **Lessaigne's Test.** This is the most conclusive test for nitrogen. A freshly cut, small piece of sodium is melted in a hard-glass test-tube ; a small amount of the substance is then added on to the molten metal, and the mixture is gradually raised to a red heat. Under these conditions, the nitrogen and the carbon of the compound combine with sodium to form sodium cyanide :

$$Na + C + N \longrightarrow NaCN$$

---

[1] Many organic substances (*e.g.*, starch, sugar, etc.) either char or burn with a smoky flame when heated on a platinum foil, or in a porcelain crucible, owing to the liberation of free carbon.

The tube, while still hot, is plunged into some distilled water in an evaporating basin. The liquid is boiled, filtered, and tested for the cyanide radical as follows :

Its reaction towards litmus paper is first noted, which should be alkaline, owing to the formation of sodium hydroxide by the action of water on the excess of sodium used in the experiment. The alkaline solution is warmed with a few drops of ferrous sulphate and a little ferric chloride, and then rendered acidic with concentrated hydrochloric acid. The formation of a blue precipitate, or a green coloration, proves the presence of cyanide in the solution and, therefore, of nitrogen in the given organic compound.

The explanation of the above test for a cyanide is that ferrous hydroxide produced by the action of sodium hydroxide on the ferrous salt reacts with the cyanide to produce sodium ferrocyanide,

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow 2NaOH + Na_4Fe(CN)_6$$

which, with the ferric salt, gives a precipitate of ferric ferrocyanide, when the solution is acidified :

$$4FeCl_3 + 3Na_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

When testing for nitrogen in a substancce which also contains sulphur, we must use a much larger quantity of sodium than that employed ordinarily (for 0·02 gm. of the substance use 0·2 gm. sodium). This prevents the formation of sodium sulphocyanide.

When testing easily volatile substances for nitrogen, the heating must be very gradual and prolonged. Further, the tube employed must be much longer, so that the portion of the substance condensing in the upper, cool part of the tube flows back on to the heated sodium.

(2) **Evolution of Nitrogen.** Substances, such as the diazo-compounds, which lose nitrogen at moderate temperatures cannot be tested for this element by Lassaigne's method. In such a case, the substance is heated with cupric oxide in a test-tube filled with carbon dioxide and the evolved gas led into a long tube filled with potassium hydroxide solution. If nitrogen is present, the evolved gas is not wholly absorbed by potassium hydroxide.

(3) **Soda-lime Test.** In a comparatively small number of nitrogenous substances, the presence of nitrogen can be detected by heating the substance with soda-lime. If ammonia is evolved, the presence of nitrogen in the substance is proved. Should, however, the test be negative, it does *not* prove the absence of nitrogen. Nitro-compounds, for instance, do not respond to this test.

Expt. 2. *Lassaigne's Test.* Take a pea-size piece of metallic sodium in a 2-inch, hard glass test-tube. Fix the tube in an iron stand, as shown in Fig. 2. Melt the sodium, and drop a *small* quantity of urea on to the molten metal. Heat the tube gradually and finally raise the temperature to bright redness. Break the hot tube, in about 10 ml. of distilled water contained in a dish. Stir up the liquid with a glass rod and filter. To the filtrate add a few drops of ferrous sulphate solution and a drop or two of ferric chloride. If the liquid be alkaline, a green precipitate of ferrous hydroxide will be produced at this stage. If no precipitate is formed, make the liquid alkaline with sodium hydroxide solution. Heat to boiling, add a few drops of ferric chloride solution and then acidify with hydrochloric acid. Formation of a blue precipitate, or a green coloration, proves the presence of nitrogen in the substance.

Expt. 3. *Soda-lime Test.* Heat some urea or thiourea with soda-lime in a test-tube. Test the evolved gas for ammonia with litmus or turmeric paper. Show that no ammonia is evolved when dinitrobenzene is heated with soda-lime.

6. Detection of Sulphur.—(1) Lassaigne's Test. This is applied in exactly the same manner as for nitrogen. The sulphur is converted into sodium sulphide, which is detected as given in Expt. 4.

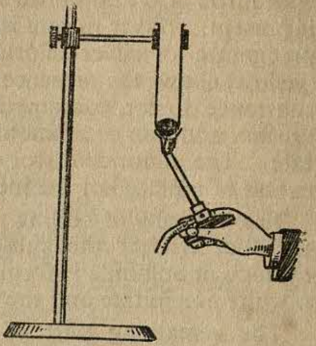


Fig. 2. Lassaigne's test for nitrogen, sulphur and halogens.

Expt. 4. Fuse thiourea or sulphanilic acid with metallic sodium as in Expt. 2. Extract the fused mass with water, and filter. Test the filtrate as follows:

(*i*) To a few drops of it add a freshly prepared solution of sodium nitroprusside: a transient, violet coloration.

(*ii*) Acidify a few drops with acetic acid, and add lead acetate; a heavy black precipitate or a dark coloration.

(2) **Oxidation to Sulphuric acid.** Easily volatile substances usually do not respond to Lassaigne's test. They are heated at 200° to 300°C with fuming nitric acid in a "bomb-tube" (see the quantitative estimation of sulphur, Chapter 3). Under these conditions sulphur gets oxidized to sulphuric acid, the formation of which is detected by the barium chloride test.

7. Detection of Halogens.—(1) Beilstein's Test. By means of this test the presence of a halogen in an organic substance can be detected quickly and conveniently. A piece of copper wire is heated in the oxidizing flame, until it ceases to impart a green colour to the flame. It is then taken out of the flame, and a minute particle of the substance containing halogen is placed on it. The heating in the flame is repeated. At first a luminous flame may be produced, owing to the burning of carbon. This is soon followed by a green or bluish green coloration, owing to the vaporization of the cupric halide.

Beilstein's test, though very simple and delicate, cannot be applied in the presence of acids and traces of metallic halides. It is also given by certain compounds containing no halogen, *e.g.*, urea, a volatile cupric cyanide being produced in this particular case. Further, the test does not differentiate the halogens. In case of doubt, or when it is desired to identify the halogen present, the following test is applied.

(2) **Lassaigne's Test.** In this test the substance is heated with sodium as in the detection of nitrogen. The fused mass is extracted

with water and the solution filtered. The filtrate is strongly acidified with nitric acid and boiled so as to decompose the cyanide or sulphide, if present. Silver nitrate is then added to a part of the filtrate. A precipitate of silver chloride (white), bromide (pale yellow) or iodide (yellow) shows the presence of chlorine, bromine or iodine in the substance under examination. Further confirmation is provided by *gradual* addition of ammonium hydroxide to the silver halide precipitate. The chloride dissolves readily ; bromide dissolves only in large excess of ammonia ; the iodide is altogether insoluble.

The necessity of boiling the filtrate with nitric acid arises out of the fact that if the substance contains nitrogen or sulphur, sodium cyanide or sulphide is formed. The former gives with silver nitrate a white precipitate and the latter a black precipitate.

The remaining part of the filtrate may be tested with 2 drops of carbon disulphide and a few drops of potassium permanganate solution. An orange-red colour in the carbon disulphide layer proves the presence of bromine ; a violet colour shows the presence of iodine.

Expt. 5. *Beilstein's Test.* Show by means of this test that cane-sugar contains no halogen. Also show that chloroform and dibromobenzene contain halogen. Further, show that the test is positive when urea (a compound containing *no halogen*) is employed.

Expt. 6. *Lassaigne's Test.* By Lassaigne's test show that chloroaniline (or quinine hydrochloride) contains a halogen : Note that the precipitate formed with silver nitrate is turned violet on exposure to light and is readily soluble in cold dilute ammonia. Hence, the halogen present is chlorine.

8. Detection of Phosphorus.—The presence of phosphorus in an organic substance can be determined by heating it with (*a*) fuming nitric acid under pressure, (*b*) sodium peroxide, or (*c*) a mixture of sodium carbonate and sodium nitrate. The phosphorus is thus oxidized to phosphoric acid or sodium phosphate, which is tested with ammonium molybdate in the usual manner.

9. Detection of Metals.—To identity the metal present in an organic substance, the latter is ignited on a piece of platinum foil. The residue is then examined for the common metallic radicals by the usual methods of inorganic analysis.

QUESTIONS

1. What do you understand by *elementary qualitative analysis* and *identification* of an organic compound ? In what essential respects does qualitative organic analysis differ from qualitative inorganic analysis ?

2. Give an account of the methods by which the presence of nitrogen, chlorine and sulphur is tested in organic solids. (*Madras, B.Sc.*)

3. How would you test an organic compound for the presence in it of (*a*) Hydrogen, (*b*) Nitrogen, (*c*) Sulphur, (*d*) Halogen, and (*e*) Oxygen ? (*Punjab, B.Sc.*)

4. Describe with practical details the methods for the identification of :
   (*i*) Nitrogen in an *unstable* organic substance.
   (*ii*) Sulphur in a readily volatile organic compound.
   (*iii*) Bromine in an organic substance that also contains nitrogen.

5. How would you identify a halogen and nitrogen when present together in an organic compound ? (*Rajasthan, B.Sc., 1953*)

CHAPTER THREE

QUANTITATIVE ELEMENTARY ANALYSIS

1. Estimation of Carbon and Hydrogen.—(**Liebig's Method**). Carbon and hydrogen are always estimated in one operation. The method employed consists in oxidizing, by means of cupric oxide, a known weight of the pure, dry substance and weighing the two products, namely, water and carbon dioxide. The process is known as **combustion**, and is carried out in a current of dry oxygen or carbon dioxide-free air.

Apparatus. For the purpose of description it is convenient to divide the apparatus into the following three parts :—

(1) **Apparatus for Delivering and Purifying Air and Oxygen.** This consists of the following :—

(*i*) Two reservoirs, one containing oxygen and the other air.

(*ii*) Two towers, one containing solid potassium hydroxide and the other fused calcium chloride, connected to each of the reservoirs.

(*iii*) A bubbler, which is a small bottle or bulb-tube containing a few drops of concentrated sulphuric acid. This serves to show the rate at which the air or oxygen is passed through the apparatus.

(2) **Apparatus for Combustion.** This consists of the following :—

(*i*) A *combustion furance* (Fig. 1), which is about 75 cm. long and has a row of burners, each provided with a tap, so that parts of the

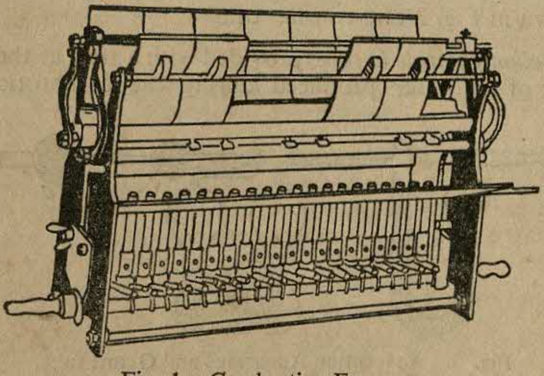


Fig. 1. Combustion Furnace.

combustion tube could be heated as desired. Above the burners is a long iron tray, on which the combustion tube is placed and which serves to protect the tube from direct contact with the flames. The top of the furnace is provided with a number of tiles. These can be lowered over or raised from above the tube as desired and thus serve to increase or decrease the intensity of heating.

(*iii*) *The Combustion Tube.* This is a hard-glass tube open at both ends, and is about 10 cm. longer than the furnace. It is first cleaned and dried and then filled with dry, ignited, wire-form cupric oxide to a length of 30 cm. (as shown in Fig. 2). The cupric oxide is kept in position by a short, tightly-fitting roll of copper gauze. The 15 cm. copper roll is also put into position as in the figure, while the space (10 cm.) meant for the boat is kept free.

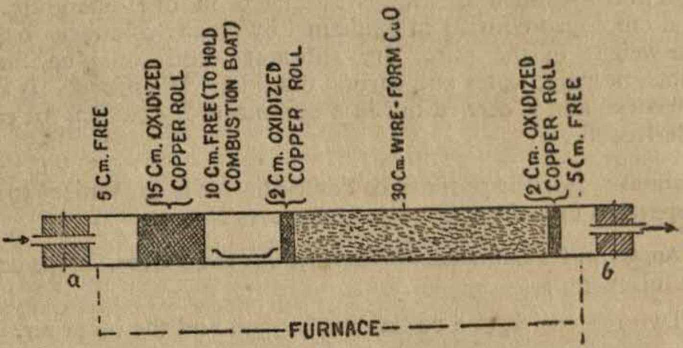

5 Cm. FREE
15 Cm. OXIDIZED COPPER ROLL
10 Cm. FREE (TO HOLD COMBUSTION BOAT)
2 Cm. OXIDIZED COPPER ROLL
30 Cm. WIRE-FORM CuO
2 Cm. OXIDIZED COPPER ROLL
5 Cm. FREE
a
b
FURNACE

Fig. 2. Methods of filling the Combustion Tube.

(3) **Apparatus for Collecting and Weighing the Water and Carbon Dioxide.** This is shown in Fig. 3 and consists of :—

(*i*) A *Calcium chloride U-tube*, provided with a trap at the side. The greater part of the water produced during the combustion collects in the trap, while the rest is absorbed by the calcium chloride. Nowadays, there is a tendency to using pumice stone soaked in concentrated sulphuric acid instead of fused calcium chloride.

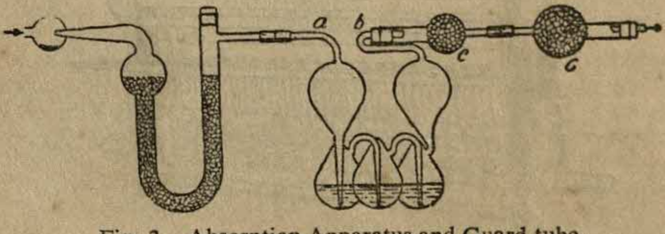


Fig. 3. Absorption Apparatus and Guard tube.

(*ii*) *Potash bulbs*, three-fourth filled with concentrated potassium hydroxide solution (1 : 1·5). This is effected by dipping the end *a* into the solution and *gently* sucking at the end *b* (Fig. 3) by means of a piece of rubber tubing, an empty wash-bottle being interposed between the mouth and the potash bulbs to prevent the passage of the liquid into the mouth. Attached to the bulbs is a horizontal tube *c*, which is filled with small pieces of solid potassium hydroxide. The later serves to catch moisture carried away by the gas during its passage through the potassium hydroxide solution, and, further, retains any carbon dioxide that might escape absorption in the bulbs. Soda-lime is sometimes preferred to aqueous potassium hydroxide, as it absorbs carbon dioxide more quickly.

(*iii*) A *guard tube*, *G*, containing calcium chloride, which serves to protect the side-tube, *c*, of the potash bulbs from atmospheric moisture.

The complete set-up of apparatus for the estimation of carbon and hydrogen is shown in Fig. 4.

Procedure. The procedure may be divided into three stages:—

(1) **Igniting the Cupric Oxide.** Before introducing the substances to be analysed and making a connection with the absorption apparatus, it is absolutely necessary to ignite the cupric oxide. This is brought about by gradually lighting all the burners beneath the combustion tube, and passing a slow current of pure dry air through it. The water that may condense at the forward cool end, *b*, of the tube is removed with a piece of filter paper wrapped round a glass rod. When no more moisture collects, the front end *b* of the tube is closed with a rubber bung carrying a calcium chloride tube. After about half an hour's heating the burners under the oxidized copper roll, the adjacent empty space, and about 5 cm. of the wire-form cupric oxide layer that lies next, are put out, and the current of air stopped.

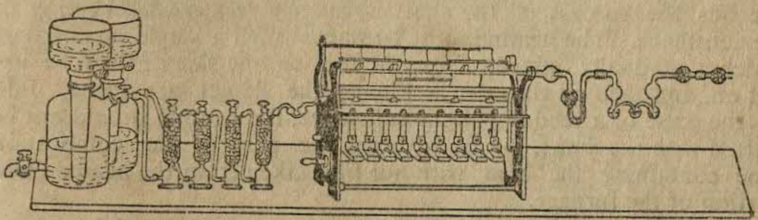


Fig. 4. Complete Apparatus for the Estimation of Carbon and Hydrogen.

(2) **Weighing the Substance and the Absorption Apparatus.** While the rear part of the tube is cooling, the substance to be analysed (about 0·2 gm.) and the two absorption vessels are weighed. The substance, unless volatile, is weighed in a porcelain boat (Fig. 5, *A*) which has

previously been ignited and cooled in a desiccator. A volatile liquid must be weighed in a small stoppered tube (Fig. 5, B) or in bulb tube (Fig. 5, C) which is sealed before weighing.

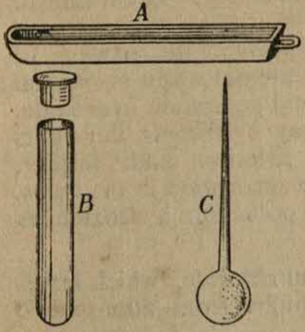


Fig. 5. Apparatus for Weighing the Substance.

(3) **Combustion.** When the rear end, *a*, of the combustion tube has cooled, the oxidized copper roll is taken out with a wire, the boat containing the weighed amount of the substance is introduced, the roll replaced, and the connection of the combustion tube with the purifying and the absorption apparatus made. In the case of a volatile liquid, the sealed-off end is filed and broken off. The bulb is then placed in the boat with its open end raised and directed towards the cupric oxide layer.

A slow current of oxygen (2 bubbles per second) is now admitted into the tube. Flames under the oxidized copper roll are just lighted, and their size gradually increased, until, finally, the spiral is brought to a dull red heat. Next, the burners under the unheated cupric oxide are gradually lighted, great care being taken not to allow any flame near the boat to become too large.

Now comes the most difficult part of the procedure, upon which depends the success of the analysis, namely *very gradual* heating of the substance. The heating must be started with a single small flame, which is gradually lighted. Next the tiles on one side of the tube are put on, and then on the other. Finally the flames are turned full. In the case of a readily volatile substance, the heating should not be started with the flame, but by covering the part of the combustion tube containing the boat with hot tiles taken from the heated front portion of the furnace.

When the burners under the boat have been burning full for about 20 minutes the combustion is regarded as being over. Any moisture that might condense near the ends of the tube is driven over into the absorption apparatus by heating with a small flame or better by a hot tile. In order to completely sweep out the products of combustion into the absorption apparatus, the rate of the passage of oxygen is somewhat increased. Finally, the oxygen in the absorption apparatus is replaced by air[1], and after allowing to cool to the room temperature, the calcium chloride tube and the potash bulb are weighed. The increase of weight in the two cases gives, respectively, the amount of water and carbon dioxide produced during the combustion.

Calculation. The method of calculation will be clear from the following example.

---

[1] If this is not done the apparent weight of the absorption apparatus will be slightly more than its actual weight.

Example 1. *On combustion, 0·210 gm. of an organic compound containing C, H and O gave 0·307 gm. of carbon dioxide and 0·127 gm. of water. What is the percentage of carbon and of hydrogen in the compound?*

Since 12 gms. of carbon yield 44 gms. of CO_2 and 2 gms. of hydrogen give 18 gms. of water, we have :—

Weight of carbon in 0·307 gm. of $CO_2 = 0{\cdot}307 \times \frac{12}{44}$ gm.

$\therefore$ Percentage of carbon $= 0{\cdot}307 \times \frac{12}{44} \times \frac{100}{0{\cdot}210} = 39{\cdot}9$.

Weight of hydrogen in 0·127 gm. of $H_2O = 0{\cdot}127 \times \frac{2}{18}$ gm.

$\therefore$ Percentage of hydrogen $= 0{\cdot}127 \times \frac{2}{18} \times \frac{100}{0{\cdot}210} = 6.7$.

2. Modifications in Carbon-Hydrogen Estimation. Complications arise in the estimation of carbon and hydrogen by Liebig's method because of the presence of certain other elements, notably nitrogen and the halogens. In such a case, a slight modification in the filling of the combustion tube becomes necessary.

(1) **When the substance contains nitrogen,** the latter is liable to be oxidized to the higher oxides, NO_2 and N_2O_3. These, being acidic, are absorbed by KOH in the bulbs, thus giving a higher value for the percentage of carbon in the compound.

This complication is remedied by placing a **spiral of reduced copper gauze** after the layer of wire-form cupric oxide. The spiral is kept **red-hot** throughout the combustion, and serves to reduce the higher oxides of nitrogen to elementary nitrogen and nitrous oxide, which are not absorbed by KOH.

(2) **When the substance contains a halogen,** the cupric halide formed in the course of analysis loses a part of the halogen on heating and is also volatile to a certain extent. The halogen and the cupric halide would be caught up by the absorption apparatus, and thus spoil the results of analysis. To meet this difficulty, a **spiral of silver gauze** is placed in the combustion tube after the layer of wire-form cupric oxide. It serves to retain the halogens and the volatile cupric halides as silver halides, which are stable towards heat.

(3) **When the substance contains a halogen, sulphur, or phosphorus,** the usual practice is to use lumps of fused lead chromate instead of cupric oxide. Lead chromate acts as a powerful oxidizing agent at high temperatures :

$$2PbCrO_4 \longrightarrow 2Pb + Cr_2O_3 + 5O$$

It has a distinct advantage over cupric oxide, as the salts of lead (namely the halides, the sulphate, and the phosphate) are far less volatile and much more stable than the corresponding salts of copper.

3. Dennstedt's Method.—This method was introduced in 1906, and is now employed in many laboratories. It has an advantage over Liebig's method in that no combustion furnace is required and a great saving of gas is effected. The principle underlying this method consists in passing a mixture of oxygen and the vaporised substance over a catalyst, consisting of platinum, platinized quartz, or platinized asbestos. Water and carbon dioxide are caught in weighed tubes containing calcium chloride and soda-lime respectively.

In case the substance under examination contains *nitrogen* or *sulphur*, it yields, in addition, NO_2 in the former case and a mixture of SO_2 and SO_3 in the latter. Before being admitted into the absorption apparatus, the gases are passed over heated lead dioxide, which absorbs NO_2, forming lead nitrate, and also SO_2 and SO_3, forming lead sulphate. The last named substance can be separated and weighed. Thus it is possible to estimate carbon, hydrogen and sulphur in one operation.

If the organic substance contains both nitrogen and halogen (*e.g.*, substituted quaternary ammonium and azonium halides) the products of combustion are passed over a heated silver spiral contained in a porcelain boat, placed in the front part of the tube. The oxides of nitrogen are thus reduced to free nitrogen which escapes. The halogen is retained by silver. The gain in weight of the porcelain boat gives the weight of the halogen. Carbon, hydrogen and halogen are estimated in one operation in this way.

4. Estimation of Oxygen.—Until recently, the percentage of oxygen in an organic substance was found *indirectly* by subtracting the sum of the percentages of all the other elements present from 100, as no direct method of estimating oxygen was available.

This procedure had its shortcomings. Firstly, the presence of an element had sometimes been overlooked and the proportion of oxygen, therefore, over-estimated. Secondly, the results offered no check on the accuracy of the analysis. Thirdly, the figure for oxygen carried an inaccuracy equal to the sum of the errors of all the determinations.

Ter Meulen's Method.—

H. Ter Meulen has worked out a method for the direct estimation of oxygen. The substance is heated in a current of dry hydrogen, and the vapours evolved first pass over *red hot platinized* asbestos, whereby the oxygen of the organic substance is converted into CO, CO_2 and water vapour. This mixture, along with excess of hydrogen, next passes over a contact catalyst (*finely divided nickel on thorium oxide*) heated at 350°. The oxides of carbon are thereby reduced and their oxygen content converted into water vapour (Sabatier and Senderens reaction) :—

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O + 59{\cdot}7 \text{ kilo-cal.}$$
$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O + 60{\cdot}4 \text{ kilo-cal.}$$

The water vapour is absorbed in a calcium chloride tube and weighed.

Aluise's Method(1947).—

The most satisfactory method for the direct estimation of oxygen so far discovered is due to Aluise and co-workers. The compound under investigation is subjected to pyrolysis in a current of dry nitrogen. The products of pyrolysis are passed over carbon heated at 1120°C, whereby all the oxygen present therein is converted into carbon monoxide. The carbon monoxide present in the gaseous mixture is then estimated by passage over iodine pentoxide and titrating the liberated iodine with standard sodium thiosulphate.

$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$$

5. Estimation of Nitrogen.—There are two different methods in general use for the estimation of this element :—

(1) **Dumas' Method.** This method consists in "combusting" the substance with cupric oxide in a current of carbon dioxide, decomposing any oxides of nitrogen formed, by passing the gases over a heated spiral of metallic copper, and collecting the nitrogen over a strong solution of potassium hydroxide. The apparatus employed is shown in Fig. 6. It consists of (*i*) a combustion tube open at both ends, and about 10 cm. longer than the bed of the combustion furnace to be used, (*ii*) CO_2 generator which generally consists of a hard glass tube charged with sodium bicarbonate, (*iii*) a **nitrometer**, which consists of a graduated glass tube, provided at the top with a funnel and a tap, and at the base with a mercury trap and a levelling bulb, and (*iv*) a "bubbler", *i.e.*, a small size gas-washing bottle containing some concentrated sulphuric acid which is interposed between the CO_2 generator and the combustion tube, and serves to show the rate at which the gas is passing.

The nitrometer is charged with 50 per cent solution of potassium hydroxide, and the combustion tube is filled as shown in the figure.

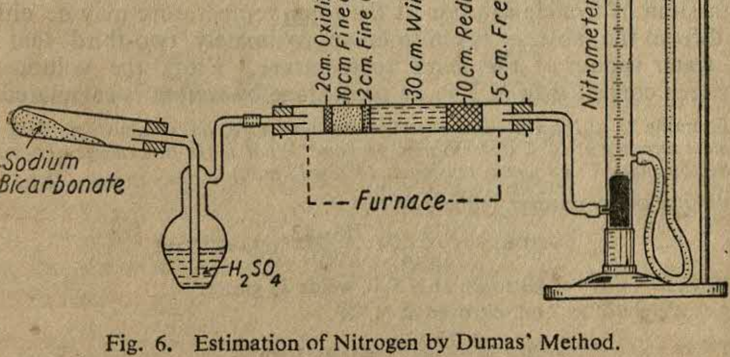


Fig. 6. Estimation of Nitrogen by Dumas' Method.

A weighed amount of the substance is intimately mixed with fine cupric oxide, and the mixture is introduced into the tube through a funnel. The mortar is rinsed out several times with small quantities of fine cupric oxide, and the rinsings also introduced into the tube. The weight of the substance taken should be sufficient to give 30 to 40 ml. of nitrogen. The copper coil in the front end of the tube is reduced by heating it strongly in a blowpipe flame and dropping it into a test-tube containing a few drops of methyl alcohol, which is then removed by placing the coil under reduced pressure. Before being used, cupric oxide should be strongly ignited, in order to remove all organic nitrogenous matter. The coil in the back end of the tube is oxidized by strongly igniting it in air.

After being properly filled, the tube is placed in the furnace and connected to the CO_2 generator and the nitrometer. The solution in the nitrometer is run out by opening the tap and lowering the levelling bulb. The tube containing sodium bicarbonate is now heated to obtain a fairly rapid current of carbon dioxide, which drives the air out of the apparatus. The issuing gas is tested from time to time by filling the nitrometer with potassium hydroxide solution. When the air in the apparatus has been completely expelled, as shown by the gas bubbles being completely absorbed by the alkali solution in the nitrometer, the latter is completely filled with potassium hydroxide solution, and the heating of the combustion tube started as follows:—

First the burners are lighted from the nitrometer end to about 6 inches of the substance. When this part of the tube is at a dull red heat, the heating is commenced from the other end, and gradually extended towards the substance. At this stage, the passage of carbon dioxide will have to be slowed down. The heating of the bicarbonate end of the substance should be so controlled that the gas enters into the nitrometer in a regular stream (about 2 bubbles per second). Towards the end, the stream of carbon dioxide will, of course, have to be again increased. When the gas bubbles are being once again completely absorbed the combustion may be taken to be over. The nitrometer is now disconnected, the gas is allowed to cool down to the room temperature, and its volume recorded. After reading the barometer, the volume is reduced to N.T.P. The tension of 50 per cent potassium hydroxide solution at the room temperature may be either read from the table, or taken to be approximately two-third that of the water vapour at the same temperature. From the volume of nitrogen corrected to N.T.P. its percentage by weight is calculated.

Example 2. *0·188 gm. of an organic compound gave, on combustion, 31·8 ml. of moist nitrogen at 14°C and 758 mm. pressure. What is the percentage of nitrogen in the compound?* (*Aqueous tension at 14°C=12 mm.*)

Volume of dry nitrogen reduced to N.T.P.

$$=31{\cdot}8\times\frac{273}{273+14}\times\frac{758-12}{760}\text{ ml.}=29{\cdot}7\text{ ml.}$$

Now, 22·4 litres of Nitrogen at N.T.P. weigh 28 grams.

∴ Weight of 29·7 ml. nitrogen at N.T.P.

$$=28\times\frac{29{\cdot}7}{22{\cdot}4\times1000}=0{\cdot}0371\text{ gm.}$$

Percentage of nitrogen in the compound

$$=0\ 0371 \times \frac{100}{0{\cdot}188} = 19{\cdot}7$$

(2) **Kjeldahl's Method.** This method consists in heating the substance with concentrated sulphuric acid and potassium sulphate. The latter serves to raise the boiling point of the liquid and thus facilitates the oxidation of the substance by sulphuric acid. A small quantity of mercury, mercuric oxide, manganese dioxide, or cupric sulphate is also added to facilitate oxidation. Carbon and hydrogen of the substance get oxidized to water and carbon dioxide respectively, while the nitrogen is converted into ammonia, which combines with the excess of the acid present to form ammonium sulphate. After the reaction is over, the mixture is distilled with an excess of sodium hydroxide solution and the ammonia set free is estimated by absorbing it in a measured excess of standard acid.

The method gives good results with amines, ammonium compounds, amino-acids, proteins and related compounds, pyridine and quinoline derivatives, and alkaloids. It is employed particularly in agricultural laboratories for the analysis of food-stuffs, manures and other products. In analysing nitro-, azo- or azoxy-compounds and nitrates, to nitrites, the substance must be reduced before submitting the same to kjeldahlizing.

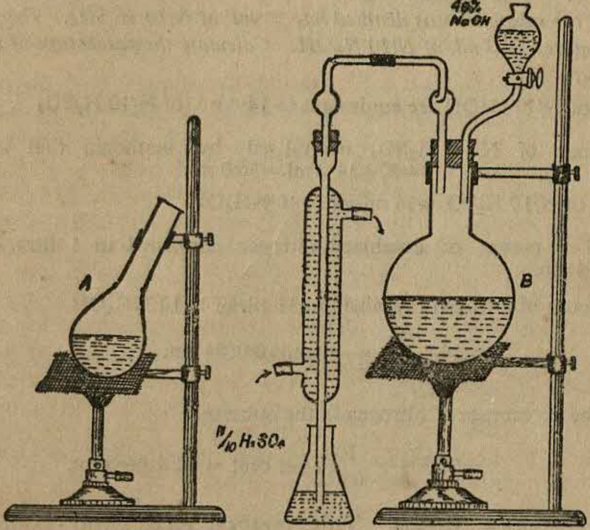


Fig. 7. Kjedahl's method for the estimation of nitrogen.

An accurately weighed quantity (about 0·5 gm.) of the finely powdered substance together with about 20 ml. of pure concentrated sulphuric acid, about 10 gm. of anhydrous potassium sulphate and a small crystal of copper sulphate, is heated in a Kjeldahl flask (Fig. 7 *A*). Since large quantities of sulphur dioxide are evolved, the heating must be conducted in a fume-closet. The completion of the process is indicated by the reaction mixture (which first turns very dark) becoming clear and colourless.

The reaction mixture, after it has cooled somewhat, is transferred together with rinsings, to a round-bottom flask provided with a tap-funnel and connected, through a trap and a vertical condenser, with a conical flask containing a measured volume (50 ml.) of N/10 H_2SO_4 (See Fig. 7 B). An excess of caustic soda solution (40 grams of NaOH in 100 ml. of water) is run in from the tap-funnel, and the mixture boiled for about half an hour. At the end of this time, the excess of the acid in the conical flask is titrated with N/10 sodium hydroxide, using methyl orange as indicator.

Example 3. *In a Kjeldahl nitrogen estimation the ammonia resulting from 0·442 gm. of the substance was distilled into 50 ml. of N/10 H_2SO_4. The excess of the acid required 14·0 ml. of N/10 NaOH. Calculate the percentage of nitrogen in the substance.*

14·0 ml. of N/10 NaOH are equivalent to 14·0 ml. of N/10 H_2SO_4

∴ Volume of N/10 H_2SO_4 neutralized by ammonia that is evolved $=50-14{\cdot}0$ ml. $=36{\cdot}0$ ml.

36 ml. of N/10 $H_2SO_4 \equiv$ 36 ml. of N/10 NH_4OH

Now, the amount of combined nitrogen contained in 1 litre of normal NH_4OH = 14 gm.

∴ Amount of nitrogen contained in 36 ml. of N/10 NH_4OH

$$=14\times\frac{36}{1000}\times\frac{1}{10}\text{gm.}=0{\cdot}0504\text{ gm.}$$

Hence the percentage of nitrogen in the substance

$$=0{\cdot}0504\times\frac{100}{0{\cdot}442}\text{ per cent }=\mathbf{11{\cdot}4\text{ per cent.}}$$

(3) **Ter Meulen's Method.** This method gives good results with all types of organic substances. It is nowadays preferred to Dumas' method, as the procedure here is much easier and simpler. A known weight of the substance is heated with *finelly divided nickel* in a current of hydrogen at 300—400°. All the nitrogen is converted into ammonia. This is absorbed in an excess of standard acid as in Kjeldahl's method.

6. Estimation of Halogens.—(1) **Carius' Method.** The estimation of a halogen by this method is carried out by heating the substance with fuming nitric acid in the presence of a few crystals of silver nitrate in a sealed tube. Carbon and hydrogen are oxidized to carbon dioxide and water, while the halogen forms silver halide, which is collected, washed, dried and weighed.

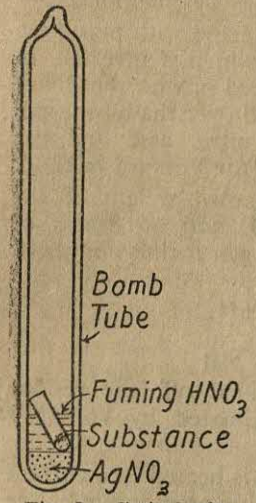


Fig. 8. Carius' tube.

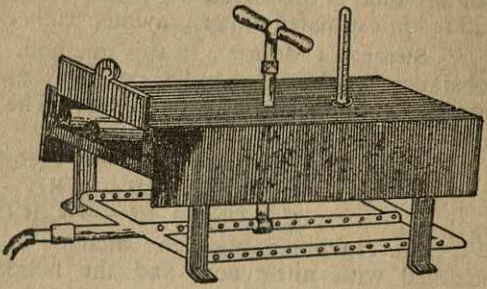


Fig. 9. Bomb furnace

The estimation is carried out in a "bomb tube"—a special Jena-glass tube with thick walls to withstand pressure. About half a gram of powdered silver nitrate and about 4 ml. of pure fuming nitric acid (*sp. gr.* 1·5) are placed in the tube, and then a small, narrow test-tube containing an accurately weighed quantity (about 0·2 gm.) of the substance is allowed to slide down into the inclined bomb tube. The test-tube will stand in the acid with its open end clear (Fig. 8). The upper end of the bomb tube is then carefully sealed off, and the tube is wrapped in an asbestos paper and heated in a bomb furnace (Fig. 9) at 150 – 200°C for about 6 hours. When the furnace has cooled down, the capillary end of the tube is carefully opened, and the contents washed out into a beaker by means of distilled water. The precipitate of silver halide is separated, dried and weighed.

Example 4. *0·369 gm. of a substance gave 0·568 gm. of AgBr. Find the percentage of bromine in the substance.*

Since 108 + 80, or 188 parts by weight of AgBr contain 80 parts of bromine, the quantity of bromine in 0·568 gm. of AgBr

$$=0{\cdot}568\times\frac{80}{188}\text{ gm.}$$

Hence, the percentage of bromine in the substance

$$=0{\cdot}568\times\frac{80}{188}\times\frac{100}{0{\cdot}369}=65{\cdot}5.$$

(2) **Other Methods.** The Carius method has certain drawbacks. Owing to high pressures developed in the tube, explosions may sometimes occur. Further, the method does not give good results with compounds containing iodine partly on account of the solubility of

silver iodide in nitric acid and partly on account of the liberation of free iodine. For these reasons, other methods for halogen estimation have been devised, of which the following may be mentioned :—

(*i*) **Peria and Schiff's Method.** The substance is mixed with pure lime and sodium (4 : 1) in a small platinum crucible, which is inverted in a larger one, the space between the two being filled in with the lime-sodium carbonate mixture. The whole is heated over the blow pipe. The product is dissolved in excess of dilute nitric acid and the halide ion estimated either gravimetrically or by the Volhard method.

(*ii*) **Stepanow's Method.** In this method, a known weight of the substance is refluxed with 98 per cent alcohol, and an excess of metallic sodium is gradually added. The halogen is thus converted into sodium halide :

$$C_2H_5OH + Na \longrightarrow C_2H_5ONa + H$$
$$RI + 2H \longrightarrow RH + HI$$
$$C_2H_5ONa + HI \longrightarrow C_2H_5OH + NaI$$

When the reaction is over, the alcohol is distilled off, the residue acidified with nitric acid and the halide estimated by Volhard's method.

(*iii*) **Ter Meulen's Method.** Here the substance is heated in a current of hydrogen and gaseous ammonia. The resulting ammonium halide is deposited on the cooler part of the tube.

7. Estimation of Sulphur and Phosphorus.—(Carius' Method). The estimation of these two elements is carried out in a manner similar to that employed in the case of halogens, but without the addition of silver nitrate. Sulphur and phosphorus get oxidized to sulphuric and phosphoric acids respectively. These are estimated as barium sulphate and ammonium phosphomolybdate as in inorganic analysis. The phosphoric acid can be estimated also by precipitation as $Mg(NH_4)PO_4$ which is then ignited and weighed as $Mg_2P_2O_7$.

8. Micro-analysis.—In certain biochemical processes, only minute quantities of valuable products are obtained which are too small to be analysed by the ordinary methods of analysis. Hence in this branch of organic research simplified methods of "micro-analysis" have been devised, which have the further advantage of effecting a saving of gas and time. A few milligrammes of the substance to be analysed are weighed on a *micro-chemical balance* and combusted by means of CuO and $PbCrO_4$ in a current of oxygen. The combustion apparatus is of a special design and is much reduced in size. The resulting CO_2 and H_2O are absorbed in the usual manner. The nitrogen is estimated volumetrically by micro-Dumas' or micro-Kjedahl's method.

QUESTIONS

1. Explain briefly with a diagram of the apparatus employed in the method of determining the percentage of carbon and hydrogen in an organic compound containing C, H and N only. (*Calcutta, B.Sc., 1945*)

2. 0·2398 gm. of an organic substance, containing only C,H, and O, gave on combustion, 0·3506 gm. of CO_2 and 0·1446 gm. of H_2O. Calculate the percentage composition of the substance. (*Ans.* C=39·9% ; A=6·7% ; O=53·4%).

3. An organic compound gave the following results on analysis :—

0·1335 gm. gave 0·2948 gm. of CO_2 and 0·0603 gm. H_2O.

0 085 gm. gave 26·4 c.c. of dry nitrogen measured at 27° and 750 mm.

Calculate the percentage of C, H and N in the substance. What reason have you to believe that the substance contains no oxygen ?

(*Ans.* C=90% ; H=5% ; N=35%)

4. Describe Kjeldahl's method for the estimation of nitrogen in organic compounds. To what important classes of organic substances is the method applicable ? (*Madras, B.Sc.*)

5. An organic compound gave the following results on analysis :—

0·197 gm. gave 0·293 gm. CO_2 and 0·150 gm. H_2O.

By Kjeldahl's method 0·59 gm. required 10 ml. of normal H_2SO_4 for the neutralization of ammonia.

(*Ans.* C=40·6% ; H=8·5% ; N=23·7% ; O=27·2%)

6. Describe in detail how you would proceed to determine carbon, hydrogen, nitrogen and sulphur in an organic compound containing these elements. (*Bombay, B Sc., 1953.*)

7. How is nitrogen, sulphur and bromine detected in an organic compound ? Explain the reactions involved in each case. How is nitrogen quantitatively determined in an organic compound ? (*Aligarh, B.Sc., 1953*)

8. Describe with experimental details two methods for the quantitative estimation of nitrogen in an organic compound. (*Andhra, B.Sc., 1952*)

9. Describe fully, with the help of suitable diagrams, the Dumas method for the estimation of nitrogen in organic compounds. (*Patna, B.Sc., 1953*)

10. Give the procedure followed in estimating sulphur and nitrogen in an organic compound. (*Poona, B.Sc., 1954*)

11. Describe with the help of suitable diagrams, the method of Dumas for the estimation of nitrogen in organic compounds. (*Aligarh, B.Sc., 1958*)

12. How would you test for the presence of bromine in an organic compound ? Describe how it is quantitatively determined. (*Rajasthan, B.Sc., 1960*)

13. Describe the method for the estimation of carbon and hydrogen in an organic compound. (*Marthwada, B.Sc., 1959*)

14. Describe with essential details the various methods available for the quantitative estimation of nitrogen in an organic compound.

0·8 gm. of a substance was digested with sulphuric acid and then distilled with an excess of caustic soda. The ammonia gas evolved was passed through 100 c.cs. of 1N sulphuric acid. The excess of acid required 80 c cs. of 1 N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the compound. (*Nagpur, B.Sc., 1960*)

[Ans. 35%]

15. How would you detect the presence of the following elements in an organic compound :—

(*a*) Nitrogen, (*b*) Sulphur, and (*c*) Chlorine.

Describe any method for the estimation of chlorine in an organic compound. (*Utkal, B.Sc., 1955*)

16. How would you detect the presence of the following elements in an organic compound :—

(*a*) Nitrogen, (*b*) Sulphur, and (*c*) Chlorine.

Describe any method for the estimation of chlorine in an organic compound. (*Gauhati, B.Sc., 1956*)

17. Describe with experimental details a method for the estimation of chlorine in an organic compound. (*Agra, B.Sc., 1958*)

CHAPTER FOUR

DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULAE

1. Calculation of Empirical Formula.—From the percentage composition of the substance, determined as given in the last chapter, the **empirical formula**, which is the simplest expression of the ratio of the atoms of different elements present in the molecule, is calculated as follows:—

(1) The percentage of each element is divided by its atomic weight to get the relative number of atoms of the various elements present.

(2) The quotients thus obtained are simplified by dividing them by the lowest value. The figures obtained either already are, or may be reduced to, whole numbers, which express the simplest ratio of atoms of the various elements present.

Example 1. *The analysis of a substance containing carbon, hydrogen and oxygen, gave the following results—*

$C=68{\cdot}84\%$; $H=4{\cdot}92\%$ and ; O (by difference) $=26{\cdot}24\%$. Calculate the empirical formula.

Dividing the percentage of each element by its atomic weight we get the atomic ratio :

$$C = \frac{68{\cdot}84}{12}=5{\cdot}74\,;\; H=\frac{4{\cdot}92}{1}=4{\cdot}92\,;\; O=\frac{26{\cdot}24}{16}=1{\cdot}64$$

Dividing by the smallest number, 1·64, we get the simplest atomic ratio : $C=3{\cdot}5$, $H=3$, $O=1$.

Hence the empirical formula of the substance is $\mathbf{C_7H_6O_2}$.

2. Determination of Molecular Formula.—To determine the molecular formula of a substance we must know : (1) the empirical formula, and (2) the molecular weight. The molecular weight is divided by the empirical formula weight to get the nearest whole number. The empirical formula is then multiplied by this number to get the molecular formula.

To take a specific example, analysis shows the empirical formula of acetic acid to be CH_2O. Its molecular weight is found to be 60. We have :

$$(CH_2O)_n=60\,;\ \text{whence}\ n=2.$$

The molecular formula of acetic acid, therefore, is $(CH_2O)_2$ or $C_2H_4O_2$.

The molecular weights of organic compounds are almost invariably determined by physical methods given below. In a few cases chemical methods may also be helpful.

3. Molecular Weights of Volatile Substances.—From Avogadro's hypothesis it follows that equal volumes of different gases or vapours under similar conditions of temperature and pressures possess weights in the ratio of their molecular weights (since the number of molecules in each case is the same). Conversely a *gram molecule* (*i.e.*, the molecular weight expressed in grams) of *any* gas or vapour must occupy the same volume under similar conditions of temperature and pressure. The volume occupied by a gram-molecule of a gas at N.T.P. is termed the **gram-molecular volume** (G.M.V.), and is found to be equal to **22·4 litres.** This relation is made use of for the determination of molecular weights of gases and volatile substances. Another relation that is employed for the molecular weight determination of a substance in the gaseous state is the following:

Mol. Wt. = Vapour Density × 2.

The following are the methods that may be used for the determination of molecular weights of volatile substances.

(1) **Victor Meyer's Method.** This method is the one most commonly employed for the determination of molecular weights of volatile liquids and solids. **A known weight of the substance is made to vaporize very rapidly,** almost *instantaneously*. The vapour displaces its own volume of air which is collected over water, and measured under the atmospheric conditions of temperature and pressure.

The apparatus employed is shown in Fig. 1. The inner tube, called the **vaporizing tube**, is cleaned and dried, and an asbestos pad is placed at its bottom. It is then introduced into the **outer jacket** consisting of a round-bottom flask with a very long neck. In the jacket is put a liquid of which the boiling point is at least 20° higher than that of the substance whose vapour density is to be determined. The inner tube is corked, the end of the delivery tube is immersed under water, and the liquid in the outer tube is boiled. When the temperature has become constant (*i.e.*, when no more air bubbles escape from the delivery tube), a **graduated tube**, *G*, filled with water is inverted over the end of the delivery tube as shown in the figure. The cork is then *momentarily* removed and a weighed amount (0·1—0·2 gm.) of the substance, contained in a **tiny, stoppered bottle**, (shown separately at *S* in the figure) is introduced. Since the temperature in the tube is considerably higher than the boiling point of the substance, the latter *vaporizes rapidly* and blows the stopper out of the tiny bottle. The vapour, rising up the tube,

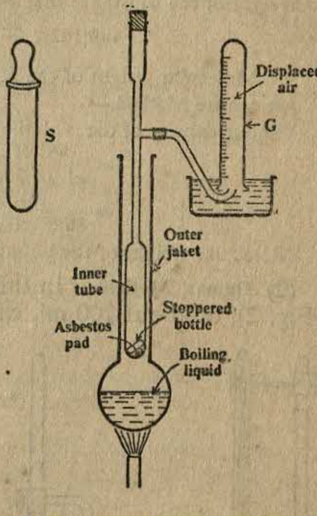


Fig. 1. Victor Meyer's apparatus.

drives its own volume of air into the measuring tube. The suddenness of vaporization and the shape of the tube are responsible for displacement of the air by the vapour of the substance.

The measuring tube is now *levelled* in a hydrometer jar containing water, and the volume of the air is noted. The temperatures of the water in the trough and the barometric pressure are also recorded.

Example 2. 0·162 *gm. of a volatile liquid displaced in a Victor Meyer apparatus,* 35 *ml. of air at* 23°C *and* 745 *mm. pressure. Calculate the molecular weight of the substance. Aqueous tension at* 23°C *is* 25 *mm. and* 1 *ml. of hydrogen and N.T.P. weighs* 0·00009 *gm.*

Barometric pressure =745 mm.
Aq. tension at 23°C =25 mm.
∴ Pressure of dry air =720 mm.
Temperature =23+273=296°A

Volume of dry air reduced to N.T.P.

$$=35\times\frac{273}{296}\times\frac{720}{760}\text{ ml.}=30{\cdot}6\text{ ml.}$$

Hence, we see that 0·162 gm. of the substance in the *vaporous* state occupies a volume of 30·6 ml. at N.T.P.

Weight of the substance that would occupy a volume of 22·4 litres at N.T.P.

$$=0{\cdot}162\times\frac{22{\cdot}4\times1000}{30{\cdot}6}\text{ gm.}=119\text{ gm.}$$

∴ Molecular weight of the liquid is **119.**

Alternative Method.—

Vapour density of the volatile liquid

$$=\frac{\text{wt. of }30{\cdot}6\text{ ml. of vapour at N.T.P.}}{\text{wt. of }30{\cdot}6\text{ ml. of hydrogen at N.T.P.}}$$

$$=\frac{0{\cdot}162}{30{\cdot}6\times{\cdot}00009}=59{\cdot}3$$

Molecular weight of the liquid is *twice* the vapour density, *i.e.*, 118·6 or **119.**

(2) **Dumas' Method.** In this method we employ a light glass bulb *B* (Fig. 2), of about 200 ml. capacity and provided with a long neck drawn out to a point. It is first weighed full of air at a known temperature and pressure, and the weight of the air. About 10 ml. of the liquid whose vapour density is to be determined, is then introduced by gently warming the bulb and holding the orifice under the liquid. The bulb is now placed in a constant temperature bath kept at a temperature at least 20° above the boiling point of the liquid under examination. A brisk ebullition takes place, and the vapour of the liquid rapidly and completely displaces the air in the bulb. When no more liquid is left in the bulb, and the pressure of the vapour, therefore, is equal to that of the atmosphere, the tip of the bulb is sealed off with a blowpipe flame.

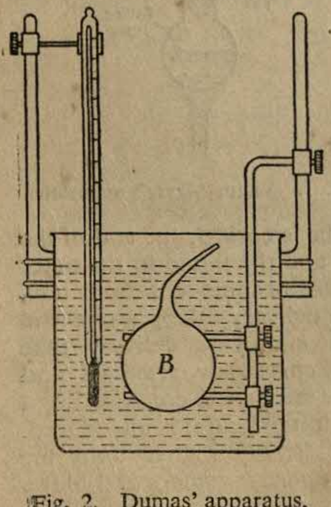


Fig. 2. Dumas' apparatus.

The bulb is now full of the vapour of the substance at the temperature of the bath and under the atmospheric pressure. It is allowed to cool and weighed.

Lastly, the capacity of the bulb is determined by breaking the end of the sealed tube under water, and weighing the bulb full of water.

(3) **Hofmann's Method.** This method is employed to determine the vapour densities, and hence the molecular weights, of substances that *decompose when vaporized under the atmospheric pressure.* The apparatus employed (Fig. 3) consists of a wide-bore barometer tube which is graduated on one side from the top downwards in millilitres. This is surrounded by a jacket through which is passed the vapour of a liquid boiling at a suitable temperature.

A small, known quantity of the substance, contained in a tiny stoppered bottle, is introduced below the mercury column in the barometer tube. The bottle rises to the top of the mercury and enters the vacuum where the vaporization of the substance takes place. When the vaporization is complete and the level of the mercury column is constant, the volume of the vapour and the depression of the mercury column are noted.

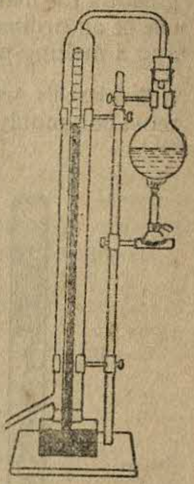


Fig. 3. Hofmann's method.

4. Molecular Weights of Non-volatile Substances.—It is of course impossible to determine the molecular weight of a non-volatile substance (such as cane-sugar) by Victor Meyer's method. In such a case the following two methods, based on the laws of osmotic pressure, are generally used. One of these methods involves the determination of the freezing-point, and the other the elevation of the boiling point of a pure solvent, caused by a given weight of a non-polar, non-volatile substance.

5. Freezing-point Method.—*It can be shown that equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same depression of the freezing-point.*

The depression of the freezing-point produced by dissolving a gram-molecule of any non-electrolyte in 100 grams of a given solvent is termed the **molecular depression** of the solvent, and is denoted by K. Now, since the depression of the freezing-point is proportional to the quantity of the solute present, if we determine experimentally the depression, $\triangle$, produced by s grams of the solute dissolved in **100 grams of the solvent**, we can readly calculate the molecular weight M, of the solute from the relation :

$$\frac{M}{s}=\frac{K}{\triangle}$$

The following table gives the freezing-points of a few common solvents and the values of K, as determined experimentally :—

The last three solvents are very useful since their melting points are above the ordinary temperature and no cooling arrangement, therefore, is necessary. The high values of their depression constants and the non-hygroscopic nature of the last two are additional advantages. Camphor is specially noteworthy, since its molecular depression is so great as to make possible the use of an ordinary thermometer and a melting-point tube.

Solvent	Freezing-point	Molecular depression (K)
Water	0°	19
Acetic Acid	17°	39
Benzene	6°	52
Phenol	40°	75
Naphthalene	80°	69
Camphor	175°	400

Beckmann's Apparatus. The Beckmann apparatus (Fig. 4) is the one most commonly used for the determination of molecular weights by the freezing-point method. It consists of the following parts :—

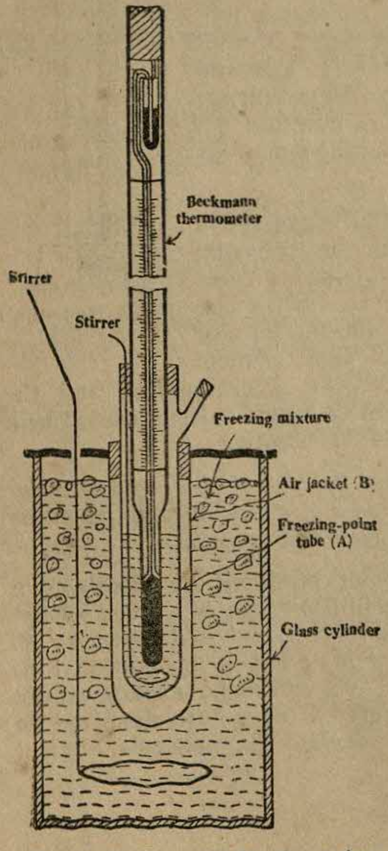


Fig. 4. **Beckmann's freezing-point apparatus.**

(1) A freezing-point tube, A, having a side-tube for introducing the solute and provided with **Beckmann thermometer** of special design and a platinum stirrer, P. The thermometer has a scale comprising 6° and reading up to one-hundredth of a degree. The quantity of mercury in the bulb can be increased or decreased as desired by handling the small reservoir of mercury at the top of the scale. This makes it possible for the thermometer to be used for solvents having widely different freezing-points.

(2) A wider tube, B, into which the freezingpoint tube is fitted. This provides an air-space round the freezing-point tube and keeps the latter from coming into direct contact with the freezing-mixture.

(3) A stout glass cylinder, filled with a suitable freezing mixture in the cover of which is fixed the outer tube, B, as shown in the figure. A stirrer, S, also passes through the cover, and serves to stir up the freezing mixture.

From 15 to 20 grams of the solvent are placed in the tube A, and weighed. The apparatus is set up as shown in the figure, and the glass cylinder is filled with a freezing-mixture at a temperature about 5° lower than the freezing-point of the solvent. The inner table, *A* is removed from the air-jacket and placed directly in the mixture until the temperature of the solvent falls about half a degree below its freezing-point. The tube is then replaced in the air-jacket and the liquid in it vigorously stirred. The crystals of the solvent begin to separate, and the temperature rises to a maximum which represents the freezing-point of the solvent. The operation is repeated to confirm the result obtained.

The tube, *A*, is now taken out of the air-jacket and a carefully weighed amount of the substance. the molecular weight of which is to be determined, is introduced through the side-tube. The liquid is stirred, in order to dissolve the substance, and the tube is put back into the air-jacket. When the liquid has become slightly super-cooled, it is stirred once again, and the *maximum* temperature reached is recorded. This gives the freezing-point of the solution. To repeat the experiment, another weighed quantity of the substance may be added to the same solution and the fresh freezing-point determined.

Example 3. *2·167 gm. and 2·833 gm. of a substance were dissolved in 100 gm. of benzene. The depressions of the freezing point were 0·348°C and 0·452°C respectively. What was the molecular weight of the substance? The molecular lowering of freezing-point of benzene is 50°C.* (*Punjab, B.Sc.*)

If M is the molecular weight of the substance, we have

$$\frac{M}{s}=\frac{K}{\triangle}$$

where $\triangle$ is the depression of the freezing point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the first experiment,

$$s=2{\cdot}167 \text{ gm.}$$
$$K=50$$
$$\triangle=0{\cdot}348°.$$

Substituting these values in the above formula, we get :

$$M=\frac{50\times2{\cdot}167}{0{\cdot}348}=311$$

Similarly, from the second experiment we have

$$M=\frac{50\times2{\cdot}833}{0{\cdot}452}=313$$

Hence, the mean value of the molecular weight from the two experiments = **312.**

6. Rast's Method of Melting Point Depression.

—An important advance in the molecular weight determination is due to Rast (1922), who, instead of a liquid solvent, used certain solid substances, **possessing very high molecular depression constants**, as solvents Some of these are tabulated below.

Solid Solvents used in Rast's Method

Solid Solvent	*Melting Point*	*Molecular Depression*
Camphor	178°*C*	400°*C*
Borneol	204°*C*	358
Hexachloro-ethane	187°*C*	477
Tetrabromo-methane	93°*C*	867
Camphene	49°*C*	311

The method is quite simple. The melting point of the pure solid solvent is first determined by the ordinary capillary tube method. Then, a homogeneous mixture of the solid solvent and the substance whose molecular weight is to be determined is made by carefully weighing out the components, melting them together to form a *homogeneous* solution, cooling the melt to the solid state, and determining its melting point by the capillary tube method as in the case of the pure solvent.

The solvent selected must fulfil the following conditions :—

(1) It must be *perfectly* miscible with the substance whose molecular weight is to be determined, and

(2) It must *not* be isomorphous with the solute.

The method of calculation, of course, is the same as in the freezing-point method of molecular weight determination.

7. Boiling point Method.—As in the case of the depression of freezing-point, it can be shown that *equimolecular quantities of different solvents dissolved in a given quantity of the same solvent produce the same elevation of the boiling-point.*

If M is the molecular weight of the substance, s the quantity of it in grams dissolved in 100 grams of the solvent, K the molecular elevation of the solvent (*i.e.*, the elevation of the boiling-point produced by dissolving a gram-molecule of any non-electrolyte in 100 gm. of the solvent), and $\triangle$ the observed elevation of the boiling-point, we have, as before :

$$\frac{M}{s}=\frac{K}{\triangle}$$

The following table gives the boiling-points and molecular elevations of the solvents ordinarily used :—

Solvent	*Boiling-point*	K	K_1
Water	100°	5·2	5·4
Ethyl alcohol	78·0°	11·5	15·6
Ether	35·6°	21·1	30·3
Benzene	80·4°	26·0	32·0
Chloroform	61·0°	36·6	27·0
Acetone	56·3°	17·2	22·2

The constants in the last but one column, K, refer to 100 grams of the solvent; those in the last column, K_1 refer to 100 ml. of the solvent at its own boiling-point. The latter are used if we measure the *volume* of the solution instead of finding its weight.

(1) **Landsberger's Apparatus.**—The most convenient apparatus to use for the boiling-point determination is due to Landsberger (Fig. 5). It consists of the following parts :—

(1) A boiling flask, F, in which the pure solvent is boiled.

(2) A bulbed inner tube, B, which is graduated in mls, and has a hole, H, just above the bulb. It is provided with (*i*) a delicate thermometer, reading up to one-tenth of a degree, and (*ii*) a delivery tube, T, which leads the vapour of the solvent from the boiling flask into the liquid placed in B. The lower end of this tube has a *rose* of small holes so as to effect a uniform distribution of the vapour through the liquid. The bulb serves to prevent portions of the liquid from being thrown out through H if the boiling becomes vigorous.

(3) An outer mantle, M, the lower end of which is connected to a

condenser, C. The vapour from the boiling liquid in B, escaping through the hole H, forms a hot jacket round B, and thus protects it from losing heat by radiation.

At first the boiling-point of the solvent is determined by placing 5 to 7 ml. of it in B and passing the vapour of the boiling solvent from F into it. As soon as the temperature has become constant (which, so far as possible, should synchronize with the bulb of the thermometer being just completely covered by the liquid), the thermometer reading is taken. The boiling is now temporarily stopped, and the greater part of the liquid in B is poured back into F, only 5 to 7 ml. being allowed to remain behind. A weighed amount of the substance whose molecular weight is to be determined is added to the solvent and the boiling point determined as before. As soon as the temperature has been read off, the flask, F, is disconnected, so that more vapour might not pass over. The thermometer and the delivery-tube are removed, and the volume of the liquid is read off, (or its weight determined). A second determination is made by passing in more of the vapour until the boiling-point is once again reached. The method of calculation is exactly similar to that given in the case of the freezing-point method.

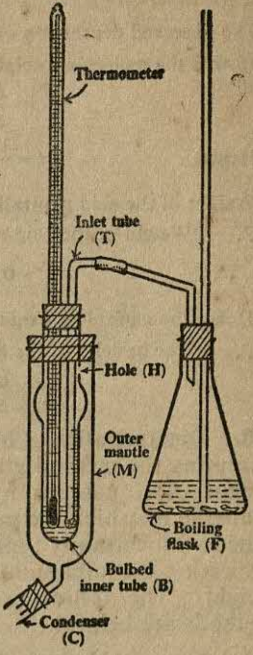


Fig. 5. Landsberger's apparatus.

Example 4. *0·562 gm. of a carefully purified substance when dissolved in 12·7 gm. of carbon disulphide ($K=23·7$) raised the boiling point of the solvent by 0·784°. Calculate the molecular weight of the substance.*

The quantity, s, of the substance present in 100 gm. of carbon disulphide

$$=\frac{0·562\times100}{12·7}\text{gm.}=4·42\text{ gm.}$$

K for carbon disulphide $=23·7$.

Elevation of the boiling point, $\triangle$, caused by 4·42 gm. of the substance dissolved in 100 gm. of carbon disulphide $=0·784°$.

If M is the molecular weight of the substance, we have :

$$\frac{M}{s}=\frac{K}{\triangle}$$

$$M=\frac{23·7\times4·42}{0·784}=134.$$

Example 5. *Freezing point of a solution of 1·392 gm. of a weak organic acid (ionization, negligible) in 20 gm. of water was found to be −1·11°. K for water = 18·5.*

0·177 gm. of the same acid neutralized 15 ml. of $N/5$ NaOH.

Calculate the basicity of the acid. (*Punjab, B.Sc., 1953*)

The quantity, s, of the acid present in 100 gm. of water

$$=1{\cdot}392 \times \frac{100}{20}\ \text{gm.} = 6{\cdot}960\ \text{gm.}$$

K for water $=18{\cdot}5$

The observed depression of the freezing-point, $\triangle = 1{\cdot}11°$

If M is the **molecular** weight of the acid, we have

$$\frac{M}{s} = \frac{K}{\triangle}$$

Hence, $$M = \frac{18{\cdot}5 \times 6{\cdot}960}{1{\cdot}11} = 116$$

Weight of the acid neutralized by 15 ml. of N/5 NaOH $=0{\cdot}177$ gm.

∴ Weight of the acid neutralized by 1 litre of normal NaOH

$$=0{\cdot}177 \times \frac{1000}{15} \times 5\ \text{gm.} = 59\ \text{gm.}$$

Hence the **equivalent** weight of the acid $=59$

∴ The **basicity** of the acid (which is always a whole number.)

$$=\frac{116}{59}\ \text{or}\ \mathbf{2}.$$

8. Determination of Molecular Formula by Chemical Methods.— Excepting the method given below for the determination of molecular weight of a gaseous hydrocarbon, no purely chemical method is available by which the molecular weight of a substance could be established with certainty ; all that we might do is to obtain information respecting the minimum value of the molecular weight or its reacting weight. The following are some important cases where chemical methods are helpful :

(*a*) **Gaseous Hydrocarbons.** The molecular formula of a gaseous hydrocarbon can be determined as follows, no previous quantitative elementary analysis being necessary :—

(1) A known volume of the gas, enclosed in a eudiometer tube, is mixed with a known excess of oxygen, and the mixture exploded. Carbon and hydrogen of the hydrocarbon burn to produce carbon dioxide and water vapour. The residual gas, consisting of carbon dioxide and unused oxygen, is allowed to cool, in order to permit the condensation of water vapour, and then its volume is noted.

(2) A strong solution of potassium hydroxide is now introduced into the eudiometer tube, which absorbs the carbon dioxide. When the absorption is complete, the volume of the gas (unused oxygen) is again noted. The different steps of the procedure are clearly shown in Fig. 6.

Calculation. The calculation of the formula of a hydrocarbon involves three steps :—

Step 1. From the experimental data, note down any two of the following volumes, and reduce them to the scale : **volume of hydrocarbon taken = 1** :—

1. Volume of carbon dioxide produced.
2. Volume of oxygen used up in the complete combustion of the hydrocarbon.
3. Contraction in volume that occurs on explosion and cooling.

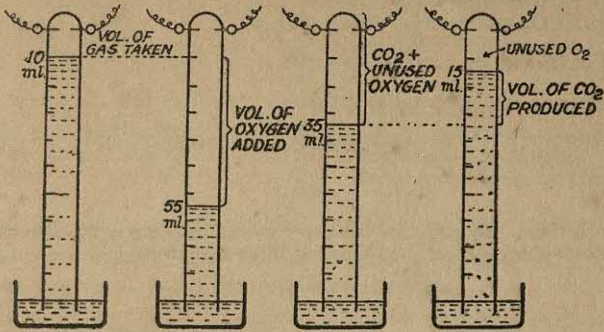


Fig. 6. Steps in the determination of the molecular formula of a gaseous hydrocarbon (Figures as in Example 6 page 55).

Step 2. Assuming the formula of the hydrocarbon to be C_xH_y, calculate the theoretical values of 1, 2 and 3 from the chemical equation[1] :

$$\underset{(1\text{ vol.})}{C_xH_y} + \underset{(x+y/4\text{ vols.})}{\left(x+\frac{y}{4}\right)O_2} \rightarrow \underset{(x\text{ vols.})}{xCO_2} + \underset{(\text{no vol.})^2}{\frac{y}{2}H_2O}$$

1. Volume of CO_2 produced $= x$
2. Volume of oxygen used up $= x+\frac{y}{4}$
3. Contraction in volume on explosion and cooling

$$=1+x+\frac{y}{4}-x-0=1+\frac{y}{4}$$

Step 3. Equate the experimental values of 1, 2 and 3 with the corresponding theoretical values, and solve any two of the equations thus obtained for x and y, as in the following examples.

Example 6. *10 ml. of a gaseous hydrocarbon and 45 ml. of oxygen were enclosed in an eudiometer over mercury and exploded. After explosion and cooling, the volume of gases was reduced to 35 ml. On addition of caustic soda there was further reduction to 15 ml What is the composition of the hydrocarbon ?*

Volume of hydrocarbon taken	=10 ml. (call it 1 vol.)
„ „ CO_2 produced	=35−15 or 20 ml. (*i.e.*, 2 vols.)
„ „ O_2 used up	=45−15 or 30 ml. (*i.e.*, 3 vols.)
Contraction on explosion and cooling	=10+45−35 ml.
	=20 ml. (*i.e.*, 2 vols.)

Theoretical Values. Let the formula of the hydrocarbon be C_xH_y. From the chemical equation,

$$\underset{(1\text{ vol.})}{C_xH_y} + \underset{(x+y/4\text{ vols.})}{\left(x+\frac{y}{4}\right)O_2} \rightarrow \underset{(x\text{ vols.})}{xCO_2} + \underset{(\text{no vol.})}{\frac{y}{2}H_2O}$$

---

[1] The expression $x+\frac{y}{4}$ in the chemical equation follows from the facts :

(*i*) The oxidation of 1 *atom* of carbon requires 1 *molecule* of oxygen ; hence x atoms of carbon will require x molecules of oxygen.

(*ii*) The oxidation of 1 *atom* of hydrogen requires half an atom or *one-fourth of a molecule* of oxygen ; hence y atoms of hydrogen will require $y/4$ molecules of oxygen.

[2] The steam produced on explosion condenses to *liquid* water on cooling, and, therefore, ceases to occupy any volume as a gas.

we get the theoretical values.

Volume of CO_2 produced $= x$ vols.

Volume of O_2 used up $= x + \frac{y}{4}$ vols.

Contraction on explosion and cooling

$$= 1 + x + \frac{y}{4} - x - 0 \text{ vols.}$$

$$= 1 + \frac{y}{4} \text{ vols.}$$

Three Equations. By equating the experimental figures with the corresponding theoretical values, we get the following three equations :—

$$x = 2 \qquad \ldots \quad (i)$$

$$x + \frac{y}{4} = 3 \qquad \ldots \quad (ii)$$

$$1 + \frac{y}{4} = 2 \qquad \ldots \quad (iii)$$

Three Methods. We may use *any two* of the equations (*i*), (*ii*) and (*iii*) at a time for calculating the values of x and y.

Method 1. Selecting equations (*i*) and (*ii*) for use, we have:

$$x = 2$$

and $\quad x + \frac{y}{4} = 3, \quad$ or $\quad 2 + \frac{y}{4} = 3, \quad$ or $\quad y = 4$

Hence, the formula of the hydrocarbon is C_2H_4.

Method 2. Selecting equations (*ii*) and (*iii*) we have :

$$x = 2$$

and $\quad 1 + \frac{y}{4} = 2$ or $y = 4$

Hence, the formula of the hydrocarbon is C_2H_4.

Method 3. Selecting equations (*ii*) and (*iii*) we have :

From equation (*iii*), $\quad y = 4$

Substituting the value of y in equation (*ii*), we have

$$x + \frac{4}{4} = 3 \quad \text{or} \quad x = 2$$

Hence, the formula of the hydrocarbon is C_2H_4.

Example 7. *20 ml. of a gaseous hydrocarbon was exploded with excess of oxygen. A volume contraction equal to 50 ml. was observed. When the residual gases were treated with KOH solution, a further volume contraction of 60 ml. was observed. What is the formula of the hydrocarbon ? The volumes of gases were measured at 0°C and 760 mm. pressure throughout.* (*Madras, 1948*)

From the experimental data we have :

Volume of hydrocarbon taken	$= 20$ ml. (call it 1 vol.)
Volume of CO_2 produced	$= 60$ ml. (*i.e.*, 3 vols.)
Volume contraction on explosion	$= 50$ ml. (*i.e.*, $2\frac{1}{2}$ vols.)

The corresponding theoretical values that follow from the chemical equation,

$$\underset{(1\text{ vol.})}{C_xH_y} + \underset{(x+y/4\text{ vols.})}{\left(x + \frac{y}{4}\right)O_2} \rightarrow \underset{(x\text{ vols.})}{xCO_2} + \underset{(\text{no vol.})}{\frac{y}{2}H_2O},$$

are :—

Volume of CO_2 produced $= x$

Volume contraction on explosion $= 1 + x + \frac{y}{4} - x$

$$= 1 + \frac{y}{4}$$

Hence, we have:

$$x=3;$$

$$1+\frac{y}{4}=2\tfrac{1}{2} \qquad \therefore \ y=6$$

Hence, the formula of the hydrocarbon is C_3H_6.

Example 8. *10 ml. of a gaseous hydrocarbon required for complete combustion 238 ml. of air (21 per cent oxygen by volume) and the gaseous products occupied 218 ml. (all volumes, being measured at N.T.P.). What is the* **empirical formula** *of the hydrocarbon?* *(Punjab, 1956)*

From the experimental data we have:

Volume of hydrocarbon taken = 10 ml. (call it 1 vol.)

Volume of oxygen required for complete combustion

$$=238\times\frac{21}{100}\text{ ml.}$$

$$=50\text{ ml. (i.e., 5 vols.)}$$

Contraction on explosion and cooling

$$=10+238-218\text{ ml.}$$

$$=30\text{ ml. (i.e., 3 vols.)}$$

The corresponding theoretical values derived from the chemical equation,

$$\underset{(1\text{ vol.})}{C_xH_y} + \underset{(x+y/4\text{ vols.})}{\left(x+\frac{y}{4}\right)O_2} \rightarrow \underset{(x\text{ vols.})}{xCO_2} + \underset{(\text{no vol.})}{\frac{y}{2}H_2O}.$$

are :—

Volume of oxygen required for complete combustion

$$=x+\frac{y}{4}$$

Contraction on explosion and cooling

$$=1+x+\frac{y}{4}-x=1+\frac{y}{4}$$

Hence, we have:

$$1+\frac{y}{4}=3; \qquad \text{whence, } y=8$$

$$x+\frac{y}{4}=5; \quad \text{or} \quad x+\frac{8}{4}=5; \ \text{whence, } x=3$$

Hence, the formula (molecular as well as empirical) is C_3H_8.

Example 9. *Find the molecular formula of a gaseous hydrocarbon from the following data:—*

18 ml. of the hydrocarbon were mixed with 108 ml of pure dry oxygen and the mixture exploded. After cooling, the volume diminished by 54 ml. On treatment of the remaining gas with a strong solution of KOH, a further contraction in volume took place, leaving 18 ml. of oxygen as residue. *(Punjab, 1951)*

Volume of hydrocarbon taken = 18 ml. (call it 1 vol.)

Volume of oxygen used up = 108 − 18 ml.

$$=90\text{ ml. (i.e., 5 vols.)}$$

Contraction on explosion and cooling = 54 ml. (*i.e.*, 3 vols.)

Let formula of the hydrocarbon be C_xH_y. The equation for the explosion reaction is :—

$$\underset{1\text{ vol.}}{C_xH_y} + \underset{(x+y/4\text{ vols.})}{\left(x+\frac{y}{4}\right)O_2} \rightarrow \underset{(x\text{ vols.})}{xCO_2} + \underset{(\text{zero vols.})}{\frac{y}{2}H_2O}$$

from which we get the following theoretical values :—

Volume of oxygen required for complete combustion of 1 volume of the hydrocarbon

$$=x+\frac{y}{4}$$

Contraction on explosion and cooling

$$=1+x+\frac{y}{4}-x=1+\frac{y}{4}$$

Equating the experimental and the theoretical values, we get :

$$x+\frac{y}{4}=5$$

and $$1+\frac{y}{4}=3$$

whence, $y=8$; $x=3$

Hence, the molecular formula of the hydrocarbon is C_3H_8.

(2) **Organic Acids.** There exists the following relation between the molecular weight of an acid, its equivalent weight and basicity:

Mol. Wt. = Eq. Wt. × Basicity

Hence, the determination of the molecular weight of an acid involves the determination of (*i*) its basicity, and (*ii*) its equivalent weight. The **basicity** of an organic acid may be found by a study of its salts and esters. Thus, acetic acid gives rise to only one series of salts and esters. It must, therefore, in all probability, be a monobasic acid. Tartaric acid from two potassium salts, a normal potassium tartrate and an acid potassium salt. It appears, therefore, to be dibasic.

The **equivalent weight** of an organic acid, may be determined either volumetrically or gravimetrically. In the **volumetric method** a suitable known weight of the acid is titrated against standard barium hydroxide, using phenolphthalein as the indicator. The result is calculated as in Example 11.

The **gravimetric method** for the determination of the equivalent weight of an acid involves the preparation of a pure sample of its silver, calcium or barium salt. The salt is then analysed to find the amount of the metal contained in a given weight of it. Silver salts are preferred for the equivalent weight determination, as they can be readily obtained pure and anhydrous, and are easily decomposed by heat to give metallic silver. A suitable quantity of the acid is dissolved in a slight excess of dilute ammonia. The excess of ammonia is then boiled off and to the *neutral* solution, thus obtained, is added a slight excess of silver nitrate. The precipitate of silver salt is washed and dried. A known weight of the salt is then carefully heated in a crucible, so as to decompose it, until a constant weight is obtained. From the weight of silver salt taken and that of metallic silver left behind the equivalent weight of the acid is calculated as in Example 10.

Example 10. *On combustion, 0·20 gram of a dibasic acid gave 0·440 gram of water and 0·195 gram of carbon dioxide. It contained no nitrogen. When 0·500 gram of its silver salt was ignited, it gave a residue of 0·355 gram of metallic silver. Find the empirical and the molecular formula of the acid.*

The empirical formula of the acid, calculated as in the usual manner, comes to CHO_2.

The equivalent weight of the silver $\text{salt} = \frac{0{\cdot}500}{0{\cdot}355} \times 108 = 152.$

Hence, the equivalent weight of the acid $= 152 - 108 + 1 = 45.$

And, since the acid is dibasic, the molecular weight is 90, which is twice the empirical formula weight. Hence, the molecular formula of the acid is $C_2H_2O_4$.

Example 11. *An organic monobasic acid gave the following combustion data :—*

0 100 gm. gave 0·2525 gm. of CO_2 and 0·0432 gm. of H_2O. 0·122 gm. of the acid required 10 ml. of N/10 barium hydroxide solution for neutralization. What is the formula of the acid ?

The percentange composition of the given acid is—

$$C = 0{\cdot}2525 \times \frac{12}{44} \times \frac{100}{0{\cdot}100} \text{ or } 68{\cdot}9$$

$$H = 0{\cdot}0432 \times \frac{2}{18} \times \frac{100}{0{\cdot}100} \text{ or } 4{\cdot}8$$

$$O = 100 - (68{\cdot}9 + 4{\cdot}8) = 26{\cdot}3$$

Dividing the percentage of each element by its atomic weight, we get the atomic ratio :

$$C = \frac{68{\cdot}9}{12} \text{ or } 5{\cdot}74 \text{ ; } H = \frac{4{\cdot}8}{1} \text{ or } 4{\cdot}8 \text{ ; } O = \frac{26{\cdot}3}{16} \text{ or } 1{\cdot}65.$$

Dividing by the smallest figure, 1·65, we get the simplest atomic ratio :

$$C = 3{\cdot}48,\ H = 2{\cdot}91,\ O = 1.$$

Hence, the empirical formula of the acid is $C_7H_6O_2$.

Empirical formula weight $= 84 + 6 + 32$ or 122.

Now, quantity of the acid neutralized by 10 ml. of N/10 $Ba(OH)_2$

$$= 0{\cdot}122 \text{ gm.}$$

∴ Quantity of the acid neutralized by one litre of normal $Ba(OH)_2$ solution, *i.e.*, the equivalent weight of the acid

$$= 0{\cdot}122 \times 100 \times 10 \text{ or } 122.$$

Since the acid is monobasic, its molecular weight is 122, which; as we have seen above, is also the empirical formula weight. Hence the molecular formula of the acid is $C_7H_6O_2$.

As the acid is monobasic and contains, therefore, only one carboxyl group, its constitutional formula must be C_6H_5COOH.

(3) **Organic Bases.** Most organic bases combine with hydrochloric acid to form salts, which, like NH_4Cl, combine with $PtCl_4$, giving sparingly soluble **platinichlorides**. The general formulae of the platinichlorides derived from mono- and di-acid bases are respectively $B'_2H_2PtCl_6$ and $B''H_2PtCl_6$, where B' and B'' represent one molecule of the monacid and the di-acid base. On being cautiously heated, the platinichlorides decompose, leaving a residue of platinum. Since the atomic weight of platinum is 195, the weight of the platinichloride that yields this amount of the metal represents its molecular weight. If the acidity of the base is known, its molecular weight can be calculated, as in the following example.

Example 12. *A monacid organic base gave the following results on analysis :—*

0·100 gm. gave 0·288 gm. CO_2 and 0·0756 gm. water.

0·200 gm. gave 21·8 ml. of nitrogen at 15°C and 760 mm.

0·400 gm. of the platinichloride left, on ignition, 0·125 gm. platinum.

What is the molecular formula of the base ? (Pt=195)

The empirical formula of the base, calculated as in the previous examples, comes to C_7H_9N.

If *B* is the molecular formula of the base, the formula of the platinichloride should be $B_2H_2PtCl_6$. A gram-molecule of the platinichloride would, on ignition, leave 195 grams of pure platinum. Hence, the molecular weight of the platinichloride, $B_2H_2PtCl_6$

$$=0{\cdot}400\times\frac{195}{0{\cdot}125}\text{ or } 624$$

∴ Molecular Weight of the base *B*

$$=\frac{624-(2+195+213)}{2}=\mathbf{107.}$$

This is identical with the empirical formula weight. Hence, the molecular formula of the base is the same as its empirical formula, *i.e.*, C_7H_9N.

Example 13. *Determine the molecular formula of a monacid base which gave the following results on analysis :—*

(*a*) *0·15 g. gave, on ignition, 0.3882 g. CO_2 and 0·1160 g. H_2O.*

(*b*) *0·35 g. gave 17·6 ml. of nitrogen at N.T.P.*

(*c*) *0·30 g. of the platinichloride gave, on ignition, 0·0686 g. platinum.*

(*C=12, O=16, N=14, Cl=35·45, Pt.=195*)

(*Punjab, B.Sc. 1960*)

From (*a*), percentage of carbon and hydrogen in the mono-acid base are—

$$C=0{\cdot}3882\times\frac{12}{44}\times\frac{100}{0{\cdot}15}=70{\cdot}58\%$$

$$H=0{\cdot}1160\times\frac{2}{18}\times\frac{100}{0{\cdot}15}=8{\cdot}58\%$$

From (*b*). percentage of nitrogen in the base is—

$$N=17{\cdot}6\times\frac{28}{22{\cdot}4\times1000}\times\frac{100}{0{\cdot}35}=6{\cdot}3\%$$

Percentage of oxygen by difference is—

$$O=100-(70{\cdot}58+8{\cdot}58+6{\cdot}3)=14{\cdot}54\%.$$

From the percentages of the elements, the empirical formula of the base works out to be $C_{13}H_{19}O_2N$.

If *B* be the molecular formula of the base, the formula of its platinichloride is $B_2H_2PtCl_6$. One gram-molecule of the platinichloride leaves on ignition 195 gm. of platinum ; hence the molecular weight of the platinichloride, $\mathbf{B_2H_2PtCl_6}$, is

$$=0{\cdot}30\times\frac{195}{0{\cdot}0686}=852{\cdot}7$$

∴ Molecular weight of the base *B*

$$=\frac{852{\cdot}7-(2+195+35{\cdot}45\times6)}{2}=\mathbf{221{\cdot}5.}$$

This weight is the same as the empirical formula weight of the base. Hence the molecular formula=the empirical formula, *i.e.*, $C_{13}H_{19}O_2N$.

(4) **Other Compounds.** Most organic substances are neither acids nor bases. In the case of such substances it is often impossible to determine the molecular weight by purely chemical methods. A detailed study of the chemical behaviour of the substance may some-

times lead to a definite conclusion. Thus, benzene (empirical formula, CH) yields a derivative having the empirical formula C_6H_5Br. Hence it follows that the benzene molecule must contain 6 (or a multiple of 6) carbon atoms, and the molecular formula must be C_6H_6 (or $C_{12}H_{12}$, $C_{18}H_{18}$, etc.) A multiple of 6, however, is out of the question, since no drivative has ever been obtained from benzene which indicates the possibility of replacing, *e.g.*, $\frac{1}{11}$th or $\frac{1}{18}$th of the total hydrogen. Hence, the formula of benzene must be C_6H_6.

9. **Law of Even Numbers.**—The general formula of saturated hydrocarbons is C_nH_{2n+2}. Hence, the molecule contains an even number of hydrogen atoms. Now, all the other organic compounds can be regarded as derived from the saturated hydrocarbons by the replacement of these hydrogen atoms by other atoms or groups, or by the removal of an even number of hydrogen atoms or by both of these causes. *Hence, the sum of the valencies of all the atoms present in the molecule of a compound must always be an even number.* Thus the molecular formula of a substance having the empirical formula C_3H_2Br must at least be twice this, since the sum of the valencies of all the atoms $(4\times3+2+1=15)$ is an odd number.

QUESTIONS

1. An organic compound gave the following results on analysis :

0·2033 gm gave on combustion 0·3780 gm. CO_2 and 0·1288 gm. water.

0·1877 gm. of the compound gave on combustion 31·7 ml. of moist nitrogen measured at 14°C and 758 mm. pressure. What is the empirical formula of the compound ? (Aqueous tension at 14°C=12 mm.) (*Punjab, 1925*)
Ans. C_3H_2NO.

2. 0·37 gm. of a substance, containing carbon, hydrogen, and oxygen, gave on combustion 0.66 gm of CO_2 and 0·27 gm. of water. Further, 0·123 gm. of the substance displaced 39·6 ml of air at 17°C and 760 mm. in Victor Meyer's apparatus. Ascertain from these data the molecular formula of the substance.
Ans. $C_3H_6O_2$. (*B.Sc., Manchester*)

3. In a determination of the molecular weight of a substance by Victor Meyer's method, 0·1680 gm. of the substance gave 49·4 ml. of vapour at 20°C and 740 mm. pressure. Calculate the molecular weight of the substance.
Ans. 83. (*Punjab, B.Sc.*)

4. 0·6 gram of a substance was dissolved in 10 gram of acetone. An elevation of 1·67°C was observed in the boiling point of the solvent. Calculate the molecular weight of the solvent. *K* for acetone is 16·7. (*Punjab, B.Sc.*)
Ans. 60.

5. 12 ml. of a gaseous hydrocarbon were mixed with 90 ml. of oxygen, and the mixture exploded. After explosion the volume was 72 ml. On adding KOH, 36 ml. of the gas disappeared, leaving oxygen only. What is the molecular formula of the gas ? All the above measurements were made at 15°C and 755 mm. pressure, the gases being saturated with moisture. (Aq. tension, at 15°C=12·7 mm.)
Ans. C_2H_6.

6. An organic tribasic acid gave the following results on analysis :

0·1584 gm. gave 0·2368 gm. CO_2 and 0·0655 gm. H_2O.

0·2219 gm. of the normal silver salt, on being carefully ignited, gave 0·1458 gm. of pure silver.

What is the molecular formula of the acid ?
Ans. $C_6H_8O_6$.

7. You are given an organic compound mixed with other substances. Outline briefly the experimental facts necessary for determining the molecular formula of the compound. *(Rajasthan, B.Sc., 1961)*

8. An organic monobasic acid gave the following combustion data :

0·100 gm. gave 0·2525 gm. of CO_2 and 0·0432 gm. of H_2O.

0·122 gm. of the acid required 10 ml. of N/10 caustic soda solution for neutralization.

What is molecular formula of the acid ? *(Punjab B.Sc., 1944)*
Ans. $C_7H_6O_2$.

9. A mono-acid organic base gave the following results on analysis :

0·100 gm. gave 0·2882 gm. CO_2 and 0·0756 gm. water.

0·200 gm. gave 21·8 ml. of nitrogen at 15°C and 760 mm.

0·400 gm. of the platinichloride left, on ignition, 0·125 gm. of platinum.

What is the molecular formula of the base ? (Pt=195 : Aqueous tension at 15°C=13 mm.) *(Punjab, B.Sc., 1934)*
Ans. C_7H_9N.

10. A monobasic organic acid gave on combustion the following percentage composition : C, 39·95 ; H, 6·69. When 0·2565 gm. of its silver salt was carefully heated, it left behind 0·1659 gm. of silver. Calculate the molecular formula of the acid. *(Andhra, B.Sc., 1942)*

11. A mono-acid organic base gave the following results on analysis :—

(*a*) 0·25 gm. of the base on combustion yielded 0·72 gm. CO_2 and 0·189 gm. H_2O.

(*b*) 0·2 gm. of the substance gave 21·80 ml. of nitrogen at 15°C and 760 mm. pressure.

(*c*) 0·8 gm. of the platinichloride, on ignition, left 0·250 gm. platinum. Calculate the molecular formula of the base. *(Aligarh, B.Sc., 1949)*

12. Describe a method for the determination of mol. wt. of an organic base. *(Agra, B.Sc., 1958)*

13. Determine the molecular formula of a monoacid base which gives the following results :

(*i*) 0·15 g. gave on ignition 0·3882 g. CO_2 and 0·1160 gm. H_2O.

(*ii*) 0·35 g. gave 17·6 ml. of N_2 at N.T.P.

(*iii*) 0·3 g. of platinichloride gave on ignition 0·0686 gm. of platinum. *(Punjab, B.Sc , 1960)*

CHAPTER FIVE

MOLECULAR STRUCTURE AND ISOMERISM

1. Isomerism.—Among inorganic compounds empirical formula in almost all cases is sufficient to characterize the substance in hand. Thus there is but one substance having the formula, $CuSO_4$, only one having the formula HCl, and so on. In organic compounds, on the other hand, even the molecular formula is not sufficiently characteristic to eliminate the possibility of confusion with other compounds. There may be many organic compounds having exactly the same molecular formula, which nevertheless differ from one another in their physical and chemical properties. Such compounds are called **isomers** or **isomerides**, the phenomenon being termed **isomerism.**

There are, for example, two different compounds having the molecular formula C_2H_6O, five having the formula C_3H_8O, and as many as eighteen having the formula C_8H_{18}. The number of isomers theoretically possible in the case of compounds having higher molecular weight may be very large indeed. Thus, there are 75 possible isomers for the molecular formula $C_{10}H_{22}$, 159 for $C_{11}H_{24}$, and 802, for $C_{13}H_{28}$. All the isomers theoretically possible in a given case, are, however, not necessarily known.

The difference in physical and chemical properties of isomeric substances is to be sought for in the internal structure of the molecules, the atoms in which are, in each case, assumed to be differently arranged. The difference of arrangement may be due—

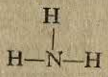
(1) To the way in which the atoms are linked with one another, without reference to their relative position in space. These are cases of **structural isomerism**, which we shall discuss presently.

(2) To the relative position of the atoms in space. These are cases of **stereoisomerism**, and will be discussed later (Chapter 7).

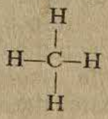
2. Molecular Structure (Kekule and Couper's Theory).—In 1858, Kekule published his famous paper "*On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon.*" In this he advanced two hypotheses upon which the modern structural formulae are based. The first of these postulated that *carbon* is *a tetravalent element* and the second that *its atoms have the capacity to link with one another.* Shortly after the appearance of Kekule's publication Couper expressed similar views in a paper published in a French scientific journal.

By the aid of the above two hypotheses we can graphically represent the molecular architecture of the majority of organic compounds. The combining capacity or *valency* of an atom is indicated by joining the symbols of the elements concerned in the union by small lines or dots, so that each line or dot represents a unit of valency. It is assumed that in the formation of a compound the valencies of the atoms undergoing combination are mutually used up. Hence the elements which, like hydrogen, are monovalent combine according to the formula H—X. Similarly, di-, tri- and tetravalent elements must combine with hydrogen as in the following :—

$H{-}O{-}H$



$\begin{array}{c} H \\ | \\ H{-}N{-}H \end{array}$



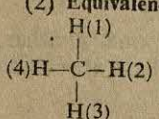
$\begin{array}{c} H \\ | \\ H{-}C{-}H \\ | \\ H \end{array}$

While in inorganic compounds elements do not always show the same valency, among organic compounds variable valency is rather the exception than the rule. The elements, carbon, hydrogen and oxygen, of which the majority of organic compounds are composed, show, in almost all cases, a valency of four, one and two respectively.

The way in which the various atoms in a molecule are linked together indicates the **structure or constitution** of the compound. It is expressed by **structural formulae** or **constitutional formulae**. In writing such formulae the following rules, based on experience, are observed.

(1) **Tetracovalency of Carbon.** The carbon atom is usually tetracovalent, and may thus combine with at the most four univalent atoms or groups. Thus in methane and carbon tetrachloride one atom of carbon is combined with four atoms of hydrogen and chlorine respectively.

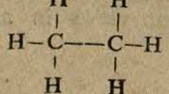
(2) **Equivalence of the four Carbon Valencies.** The four valencies of a carbon atom are equivalent to one another, since the replacement of *any* one of the four hydrogen atoms of the methane molecule by a monovalent substituent always gives the *same* product.



$\begin{array}{c} H(1) \\ | \\ (4)H{-}C{-}H(2) \\ | \\ H(3) \end{array}$

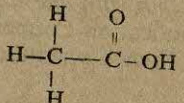
Methane

(3) **Linking of Carbon Atoms.** Carbon atoms possess a great capacity to link with one another. In the formation of carbon links, it is assumed that each carbon atom is bound by 1, 2, or 3 valencies to a neighbouring carbon atom, and the remaining valencies can then be saturated by hydrogen, oxygen, chlorine, etc. Those compounds in which only singly bound carbon atoms are present are termed **saturated compounds**, *e.g.*,



$\begin{array}{c} H \quad H \\ | \quad\; | \\ H{-}C{-}{-}C{-}H \\ | \quad\; | \\ H \quad H \end{array}$

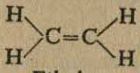
Ethane



$\begin{array}{l} \;\;\; H \quad\;\; O \\ \;\;\; | \quad\;\; \Vert \\ H{-}C{-}{-}C{-}OH \\ \;\;\; | \\ \;\;\; H \end{array}$

Acetic acid

while those containing carbon atoms linked together by double or triple bonds are called **unsaturated compounds**, *e.g.*,



Ethylene

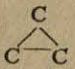
$H-C\equiv C-H$

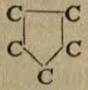
Acetylene

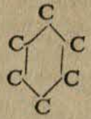
Similarly, three or more carbon atoms may link together, forming an open chain, such as

$C-C-C \qquad C-C=C-C \qquad C-C\equiv C-C$

or a closed chain or ring such as :

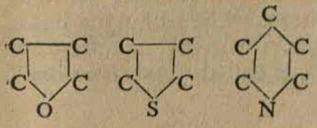




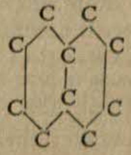


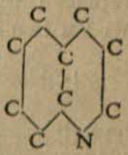
Some important open-chain compounds are present in fats and oils. For this reason, the branch of organic chemistry that deals with open-chain compounds is called the **fatty** or **aliphatic series**, and a substance belonging to this class is known as a *fatty* or an *aliphatic compound.*

Substances containing closed chains are termed **cyclic compounds.** If the rings are composed entirely of carbon atoms, they are called **carbocyclic** ; if they contain, in addition to carbon, one or more atoms of some other polyvalent element, as in cases given in the left hand margin they are termed **heterocyclic.**

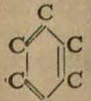


In addition to substances containing simple carbocyclic and heterocyclic rings of the above types, compounds containing two or more **condensed rings**, such as those shown in the margin, are known. In these compounds, each pair of rings possesses two carbon atoms in common.

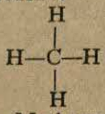




Among carbocyclic compounds those containing rings of six carbon atoms with alternate single and double bonds (*i.e.*, a closed system of 'conjugated' double bonds), as shown in the left hand margin, are of the greatest importance, and are called **aromatic compounds** or **benezene derivatives.**

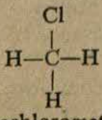


3. **Substitution.**—The atoms of the element present in the molecule of an organic substance may be replaced or *substituted* by an equivalent number of atoms of other elements. Thus, the four hydrogen atoms of methane can be successively replaced by atoms of chlorine.



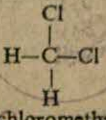
CH_4

Methane



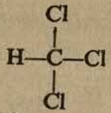
CH_3Cl

Monochloromethane



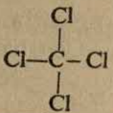
CH_2Cl_2

Dichloromethane



$$\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}$$

Trichloromethane

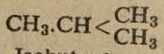


$$\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{Cl}- & \mathrm{C} & -\mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}$$

Tetrachloromethane

4. Nuclear Isomerism (*Chain Isomerism*).—If an atom of hydrogen in the **methane** molecule be replaced by a methyl group, the hydrocarbon **ethane**, $CH_3.CH_3$, is obtained. Similarly, if one of the hydrogen atoms of ethane be replaced by a methyl group, we get **propane** $CH_3.CH_2.CH_3$. Since all the hydrogen atoms of methane and also those of ethane are in a similar state of combination, there is only one ethane or propane possible. This, however, is not the case with propane, which contains hydrogen in two *different* states of combination. Hence the replacement of hydrogen by the methyl group gives, in this case, two different hydrocarbons,

(1) $CH_3.CH_2.CH_2.CH_3$ and (2)



$CH_3.CH{<}\begin{matrix}CH_3\\CH_3\end{matrix}$

Normal butane Isobutane

having the same composition, C_4H_{10}.

The cause of **isomerism in butanes**, as in numerous other compounds, is the difference in the constitution of the carbon chains. Normal butane has a *straight* chain of carbon atoms while isobutane has a *branched* chain. Isomerism of this type, involving a difference in structure of the carbon chain or nucleus, is called **"chain isomerism"** or **"nuclear isomerism"**.

5. Position Isomerism.—If a hydrogen atom of propane be replaced by an atom of chlorine or some other monovalent element, we get two different compounds :

$CH_3.CH_2.CH_2Cl$	$CH_3.CHCl.CH_3$
1-Chloropropane or Normal propyl chloride	2-Chloropropane or Isopropyl chloride

The difference between these compounds lies not in the carbon chain itself but in the different *positions* of the substituent in the same carbon chain. Isomerism of this type is therefore termed "position isomerism".

6. Homologous Series.—On comparing the formulæ of hydrocarbons derived from methane by the successive replacement of hydrogen by methyl groups, as described above, we find that each successive member of the series has one atom of carbon and two of hydrogen more than its predecessor :

CH_4	C_2H_6	C_3H_8	C_4H_{10}
Methane	Ethane	Propane	Butane

If the number of carbon atoms in the molecule of any of the above hydrocarbons be expressed by n, the number of hydrogen atoms will be found to be $2n+2$. This is true for the higher members as well. The series, therefore, possesses the **general formula** C_nH_{2n+2}.

Now if we replace a hydrogen atom in the above hydrocarbons by a hydroxyl group, we obtain the following series :

$CH_3.OH$	$C_2H_5.OH$	$C_3H_7.OH$	$C_4H_9.OH$
Methyl alcohol	Ethyl alcohol	Propyl alcohol	Butyl alcohol

Here also we find that each member of the series differs from the preceding one by CH_2, and the whole series may be expressed by the general formula $C_nH_{2n+1}.OH$.

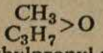
Replacement of the hydrogen of hydrocarbons by other groups or atoms always results in the formation of various series of compounds, whose successive members differ by CH_2, and which may be represented by general formulae as in the above two cases.

A group of similarly constituted compounds, any two consecutive members of which differ in molecular composition by CH_2, is termed a **homologous series**, and its various members are known as **homologues.**

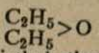
The various members of a homologous series, owing to similar molecular constitution, possess similar chemical properties; and their physical properties have been found to undergo a gradual change from member to member.

7. **Metamerism.**—This term is rarely used nowadays. It refers to a kind of structural isomerism which exists between substances of the same class, and is due to the linking of different alkyl radicals to the same polyvalent atom or group. Metamerism is exhibited by ethers, ketones, esters, amines, etc. The following few cases may be mentioned as illustrations of this type of isomerism :

$C_4H_{10}O$:—

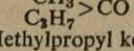

$\begin{matrix}CH_3\\C_3H_7\end{matrix}>O$

Methylpropyl ether

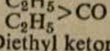

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$

Diethyl ether

$C_5H_{10}O$:—


$\begin{matrix}CH_3\\C_3H_7\end{matrix}>CO$

Methylpropyl ketone

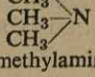

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>CO$

Diethyl ketone

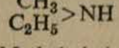
$C_4H_8O_2$:—

$CH_3COO.C_2H_5$	$C_2H_5COO.CH_3$	$HCOO.C_3H_7$
Ethyl acetate	Methylpropionate	Propyl and isopropyl formates

C_3H_9N :—


$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}>N$

Trimethylamine


$\begin{matrix}CH_3\\C_2H_5\end{matrix}>NH$

Methylethylamine

$C_3H_7.NH_2$

Propylamine and isopropylamine

8. **Saturation and Unsaturation.**—If we compare the formula of ethane, $CH_3.CH_3$, with that of ethylene, $CH_2{=}CH_2$, we see that while in the former the four valencies of each of the carbon atoms are employed in forming *single* bonds between the various atoms, in the latter there exists a *double* linkage between the two carbon atoms. Similarly, in acetylene, $CH{\equiv}CH$, the two carbon atoms are linked together by a *triple* bond.

Compounds, like ethylene and acetylene, which contain one or more pairs of carbon atoms linked together by double or triple bonds are termed *unsaturated*, while, as already stated, those in which all the carbon atoms are joined together by single bonds are said to be *saturated.* Since in the case of saturated compounds the maximum combining capacity of carbon atoms is already in action, they can form derivatives only by **substitution.** Unsaturated compounds, on the other hand, can form derivatives by direct **addition.** Thus, ethylene and acetylene combine respectively with two and four atoms of hydrogen, chlorine, etc., yielding saturated compounds :

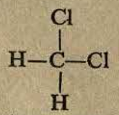
$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3.CH_3$$
$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl.CH_2Cl$$
$$CH{\equiv}CH + 2H_2 \longrightarrow CH_3.CH_3$$
$$CH{\equiv}CH + 2Cl_2 \longrightarrow CHCl_2.CHCl_2.$$

Thus, paradoxical as it may seem, carbon atoms bound together by double or triple linkages represent a more unstable state of affairs than singly bound carbon atoms. This singular behaviour has been explained by Baeyer by means of his "strain theory".

9. Molecular Models.—According to the modern concept of valency (see Sec. 15 onwards), the *single*, *double* and *triple* bonds, referred to in the preceding sections are **covalent bonds.** They are produced by the *sharing* of two, four and six electrons, respectively, between the two carbon atoms joining together. A fundamental property of such bonds is that they are **directional.** Hence the relative positions of atoms in a covalent molecule are fixed (*i.e.*, if we disregard the slight vibrational and rotational motions). Each covalent molecule, therefore, has a definite, three dimensional architectural pattern.

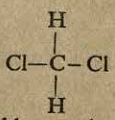
Molecular models constructed out of wooden balls and elastic steel pins are very helpful in grasping the fundamental idea of definite structure of organic molecules. The number of holes in a ball corresponds to the covalency of the element concerned, and they are so bored that the inserted pins make angles equal to those experimentally measured for the atoms represented.

Molecular models have proved very useful for explaining the phenomena of isomerism, steric hindrance and ring-formation. To take here a simple case, if the four valencies of the carbon atom all lay in one plane, we would get two dichloromethanes as shown below :—



$$H{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}{-}Cl$$

Dichloromethane
(one possibility)



$$Cl{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl$$

Dichloromethane
(second possibility)

In the first formula, the two chlorine atoms lie near to each other ; in the second they occupy opposite positions. But, as we know, *there exists only one dichloromethane.* Hence, the four valencies of the carbon atom could *not* lie in one plane and the molecules of methane, chloromethane and dichloromethane, etc., are not flat. As a matter of fact, the four atoms attached to the central carbon atom of the methane molecule are so situated that lines drawn from them to the

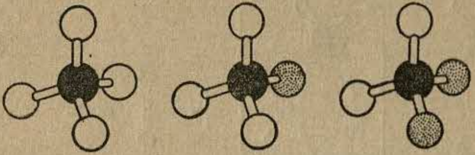


Fig. 1. Molecular models of methane (left) chloromethane (centre) and dichloromethane (right). In the drawing, the carbon atom is shown black, the hydrogen atoms white and the chlorine atoms dotted.

carbon atom make equal angles[1] in space. The molecular models shown in Fig. 1 have been constructed on this basis, and it is clear from the right-hand side model that there can exist only *one* dichloromethane.

Besides the above type of molecular models, there is another type in which a scale drawing of the balls is made according to the measured effective diameters of the atoms concerned. The balls are also cut away so that their centres come closer together. This is done with a view to representing the fact that there is an actual shortening of the distances between centres of the atoms when the latter are joined together by covalent bonds. A scale model of the chloromethane molecule is given in Fig. 2, as an illustration. The relatively large effective diameter of the chlorine atom is clear from the model.

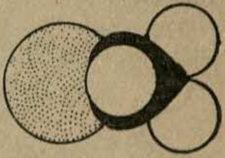


Fig. 2. Scale model of chloromethane.

10. Baeyer's Strain Theory.—According to the fundamental hypothesis of stereochemistry (chapter 8), the four valency bonds of the carbon atom are directed towards the angular points of a regular tetrahedron (at the centre of which the carbon atom is supposed to lie), and thus make an angle[1] of 109° 28′ with each other. In 1885, Baeyer pointed out that a single bond may be created between two carbon atoms without interfering with the line of action of any of the valencies of the two carbon atoms. There is, as we say, "free rotation about the single bond," *i.e.*, freedom of disposition of the six atoms or groups attached to the two carbon atoms.

On the other hand, when the two carbon atoms become doubly bound, the valencies concerned in the formation of the double bond are submitted to bending, or distortion. A definite strain is thus set up in the molecule, which renders the double bond easily attackable by reagents. The tension produced in the molecule by the creation of a double bond may be conveniently demonstrated by means of atomic models, in which the double bond is represented by a pair of flexible wires.

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[1] The calculated value of this angle is 109° 28′.

The mechanism of *addition reaction* that an unsaturated compound readily undergoes may be graphically illustrated by means of atomic models, as in Fig. 3. The combination of ethylene (*A*) with bromine is here represented as being preceded by the *rupture* of the double bond, as shown at (*B*). The product of the reaction is dibromoethane (*C*), which is a saturated compound having normally directed valencies :

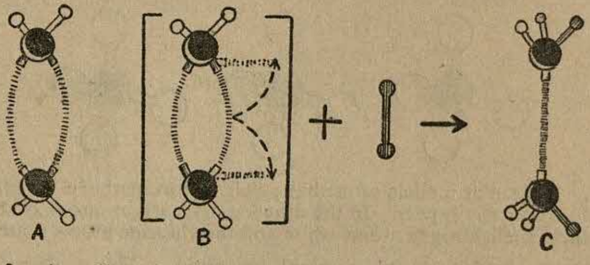


Fig. 3. Atomic-model representation of the combination of ethylene with bromine.

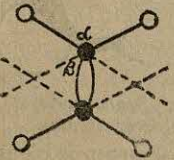
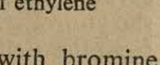


Fig. 4. Representation of Double bond by means of Atomic models
$\alpha=109^\circ\ 28'$
$\beta=54^\circ\ 44'$

The strain theory has been very helpful in explaining the **relative stability of ring systems** having different number of saturated carbon atoms. The strain produced in each case is proportional to the angle of displacement of the valency bonds from their normal positions. It is possible to calculate this distortion in various cases if we assume each axis to have undergone an equal displacement. Thus in the cyclopropane ring the carbon atoms may be supposed to be at the corners of an equilateral triangle ABC (Fig. 5). The dotted lines *AK*, and *AL*, represent the original direction of the two valency bonds of the carbon atom *A*, and the curved lines their present disposition. The original angle *a*, between the two bonds was 109° 28′, and the present angle between them is 60°. Hence, the deviation, β, undergone by each bond from its normal position

$$=\tfrac{1}{2}(109^\circ\ 28^\circ-60^\circ)=24^\circ\ 44'.$$



Similarly, in the case of a double bond (see Fig. 4) the distortion is measured by the angle, $\tfrac{1}{2}(109^\circ\ 28^\circ-0^\circ)=54^\circ\ 44'$.

The following table gives the extent of distortion in different cyclane rings, calculated as above :—

Double bond	+54° 44′	Cyclobutane	+9° 44′
Cyclopropane	+24° 44′	Cyclopentane	+0° 44′

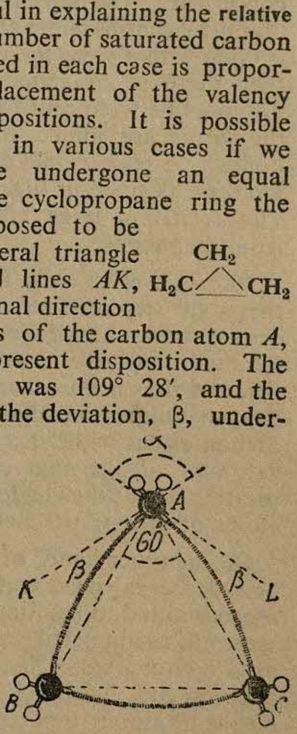


Fig. 5.
The cyclopropane ring.
$\alpha=109^\circ\ 28'$ $\beta=24^\circ\ 44'$

The cyclopentane ring, being under the least strain, is the most stable. Rings with less than five carbon atoms are progressively less stable and more reactive, until the exceedingly reactive double bond is reached.

The deductions of the strain theory are fully supported by experiment. In ethylene the strain is the maximum and the tendency to form addition compounds resulting in the destruction of the ring is the highest. The strain is much less in the case of cyclopropane, and hence the opening of the ring by means of bromine, etc., here occurs much less readily than in ethylene (see the chapter on 'Alicyclic Compounds'). Again, whereas cyclopropanecarboxylic acid is readily attacked by hydrogen bromide in the cold, cyclobutanecarboxylic acid is practically unaffected. Finally, cyclopentanecarboxylic acid are not affected even on continued boiling with hydrogen bromide.

The extent of strain set up in a carbon chain when the end carbon atoms are joined together to form a ring can be beautifully shown by means of molecular models (Fig. 6). In a 3-carbon ball model (left) it is impossible to close the ring if the connecting rods are rigid. When the connecting rods are elastic, the ring closure requires considerable pressure, and the ring produced, is under considerable strain ; it tends to fly open. With a 4-ball model (middle) the strain is much less, though it is still sufficient to make the ring system unstable. A 5-carbon model (right) offers no resistance to ring closure. There is, therefore, no strain in the ring and the system is stable.

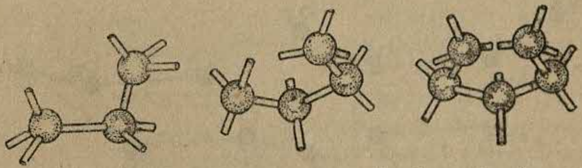


Fig. 6. Showing that the strain set up on ring formation decreases as the number of carbon atoms in the chain increases from three to five, there being practically no strain in the last case.

According to modern theory of covalency, the strain in the ring is due to *electron repulsions*. In the ethylenic bond and in 3- and 4-carbon ring systems, the electronic orbits are displaced from their normal dispositions. The greater the displacement, the greater is the strain or the tendency to return to normal. When the electronic disposition is already normal (*i.e.*, when the lines joining the four other atoms to carbon make the tetrahedral angle of 109° 28′) or nearly so, as is the case with the 5-carbon ring, there is no displacement and therefore no strain.

11. Strainless Multiplanar Rings—Sachse-Mohr Theory.—While the chemical behaviour of alicyclic compounds having a positive angle of deviation (*i.e.*, those having rings with 5 or less carbon atoms) agrees fairly well with Baeyer's strain theory, this is not the case with compounds having rings of 6 or more carbon atoms.

In the first place, the cyclohexane ring appears to be quite as stable as the cyclopentane ring; both classes of compounds refuse to react with bromine, hydrobromic acid, etc., and moreover, it is possible to convert a cyclopentane compound into a cyclohexane derivative, and *vice versa*. The cycloheptane ring should, according to Baeyer's theory, be quite as reactive as the cyclobutane ring. Actually, however, it is as stable as the cyclopentane and the cyclohexane rings. The same is true for rings containing 8 or more carbon atoms.

The remarkable stability of ring systems composed of six or more carbon atoms has been explained by assuming that the carbon atoms do *not* lie in the same plane; they are *multiplanar*. As early as 1890, Sachse suggested strain-free models for cyclohexane (Fig. 7). The theory was still further elaborated by Mohr, in 1918, so as to include all rings containing more than 5 carbon atoms. The "boat" and "chair" formulae do *not* represent two isomers, as the Sachse-Mohr theory further postulates that the two spatial configurations are readily *interconvertible*. This can be best demonstrated with the help of molecular models. The cyclohexane model will at once assume either the "boat" or the "chair" form. A recognizable, though slight, pressure will be necessary to bring the six carbon balls into one plane. The arrangement, however, will be unstable, and as soon as the pressure is released, it will easily slip into one or the other of the two forms shown in Fig. 7. Further, each of these forms will slip into the other quite readily, thus explaining why only one form of cyclohexane is possible.

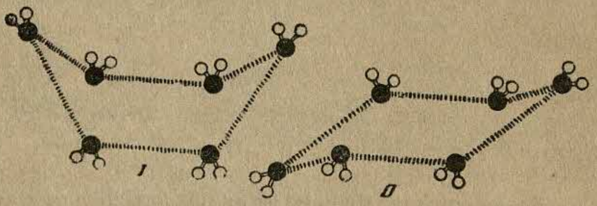


Fig. 7. "Boat" and "Chair" formulae for cyclohexane.

At the time Baeyer put forward his strain theory, only a few compounds containing rings of more than six carbon atoms were known. Baeyer held that this was due to an *outward strain*, which must exist if all the carbon atoms composing the ring lay in *one plane*. This, as we now know, is not the case. Hence, Baeyer's theory is not applicable to larger rings, which are quite as stable as the 5-carbon ring.

Ruzicka, a Swiss chemist, and his coworkers prepared (1926) cycloketones with ring-systems up to 34 carbon atoms, and have shown them to possess a high degree of stability. Many naturally occurring substances have been shown to contain large cyclane rings. The strongly odorous substances, **muscone** (from musk deer[1]) and **civetone** (from civet cat[2]) are examples of this class of compounds. They have been shown to contain 15- and 17-membered rings respectively.

12. Thiele's Theory of Partial Valency : Conjugated Double Bonds.—It was observed by Baeyer and Rupe in 1893 that when **muconic acid,**

$$HOOC.CH=CH.CH=CH.COOH,$$

is reduced, four atoms of hydrogen are not added at once, as the existence of two pairs of double bonds might lead one to expect, but that only *two* atoms are first absorbed. These attach themselves to the two carbon atoms carrying the carboxyl groups, and a new double bond comes into being between the two middle carbon atoms :

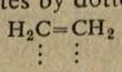
$$HOOC.CH_2.CH=CH.CH_2.COOH.$$

The resulting compound, known as **hydromuconic acid,** on being further reduced, combines with two more atoms of hydrogen, yielding *adipic acid,*

$$HOOC.CH_2.CH_2.CH_2.CH_2.COOH.$$

A system of alternating single and double bonds, as in muconic acid, is termed by Thiele **conjugated double bonds.** Many cases of **1 : 4 addition,** as in muconic acid, have been observed in compounds containing conjugated double bonds.

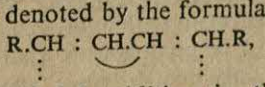
In order to explain the peculiar behaviour of such compounds Thiele put forward the hypothesis that when two atoms are united by a double bond, the whole of the affinity between them is not used up, but that there remains a slight *residual affinity* or *partial valency* on each atom. This he denotes by dotted lines, *e g.*,



$$\underset{\vdots}{H_2C}=\underset{\vdots}{CH_2}$$

He assumed that the power to form addition compounds is due to the presence of such residual affinities.

Now, in a system of conjugated double bonds there are four partial valencies. Of these, the two middle ones are regarded by Thiele to have neutralized each other, while the other two remain active. This is usually denoted by the formula,



$$R.\underset{\vdots}{CH} : \underbrace{CH.CH} : \underset{\vdots}{CH}.R,$$

which explains the usual 1:4 addition in the case of compounds having a conjugated system of double bonds.

Thiele's theory appears to give a satisfactory explanation of the behaviour of a large number of unsaturated compounds. It has been particularly helpful in showing the saturated nature of the benzene ring. More recently, however, facts have been discovered which do not agree with the rule of 1:4 addition.[1]

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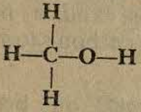
[1] Musk consists of the dried secretion of preputial follicles of the male musk deer found in the Himalayas.

[2] Found in Abyssinia.

13. Determination of Structural Formula.—After the molecular formula of a substance has been found, the organic chemist proceeds to determine the structure of its molecule. This may involve the following steps :

(1) First, we write down all the possible combinations of the constituent atoms consistent with their respective valencies.

(2) Then, out of the various possible formulæ we select one that agrees best with the properties of the compound and its methods of formation.

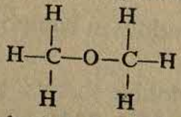


$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

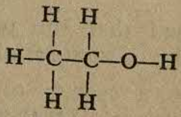
In case the number of atoms in the molecule is small, the determination of its constitution is usually a simple matter. Thus, if the valencies of carbon, hydrogen and oxygen be assumed to be 4, 1 and 2 respectively, the compound having the molecular formula CH_4O (methyl alcohol) can have only one structure as shown in the margin. Similarly, the compound of the molecular formula CH_2O (formaldehyde) must have the structure $\mathrm{H.C}{\lessgtr}^{\mathrm{H}}_{\mathrm{O.}}$ In case two or more structural formulæ are possible, we must select the right one by reference to the following :—

(*i*) The possibility of the compound being transformed into, or of its being produced from, compounds of known structure. We know it from experience that *when an atom or radical present in a molecule is replaced by another substituent, the latter, as a rule, goes into the position originally occupied by the former.*[2]

The procedure may be illustrated by reference to ethyl alcohol, C_2H_6O. As one may see by trial, there are only two ways in which the structure of the compound may be represented :

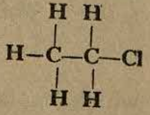
(*a*) 

$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

and (*b*) 

$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Now, ethyl alcohol may be obtained by the hydrolysis of ethyl chloride, C_2H_5Cl, and conversely, it may be converted into ethyl choride by treatment with hydrogen chloride. Hence, its structure must be analogous to that of ethyl chloride. But there is only one structure possible for the latter substance, as shown in the margin. Hence ethyl alcohol must possess the constitution (*b*) and not (*a*).



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

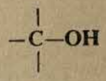
---

[1] See under Constitution of Benzene.

[2] In certain rare cases, however, the atoms or radicals "migrate" to new positions. See for instance, the *Walden Inversion.* Formation of resorcinol from benzene-*o*-disulphonic acid is another well-known example of the same phenomenon.

The conclusion thus arrived at is in complete harmony with the chemical behaviour of ethyl alcohol. Thus of the six hydrogen atoms, that the molecule contains, only *one* is replaceable by sodium ; hence this hydrogen atom must be in a different state of combination from the rest. This condition is fulfilled by the formula that we have just now selected.

(*ii*) The close similarity of the physical and chemical properties of the compound with those of another, whose constitution is known. Thus, an additional proof of ethyl alcohol as possessing the structure (*b*) is that in its entire physical and chemical behaviour it closely resembles methyl alcohol, for which there is only one structure possible, *viz.*, CH_3OH. Hence, ethyl alcohol must contain a hydroxyl group in its molecule, just as methyl alcohol does. Similarly, all other alcohols must have in their molecules the grouping shown in the margin.



$$-\overset{|}{\underset{|}{C}}-OH$$

(3) The formula finally adopted must be supported by as many reactions of the compound as possible. It must also be checked by reference to its various physical properties (see chapter 6). As the last step, an attempt is made to *synthesize* the compound from one of known structures by a series of simple reactions that the formula under consideration may suggest. Should this be successful, the formula is finally accepted as established.

14. Tautomerism.—A number of cases are known in which one and the same compound behaves as if it had *two* different structures. Thus, **hydrocyanic acid** may react as $H-C\equiv N$, or as $H-N\overset{\rightarrow}{=}C$. It gives rise to two different classes of alkyl derivatives, (*i*) the **cyanides**, derived from the first, and (*ii*) the **isocyanides**, derived from the second form. A substance which, like hydrocyanic acid, can react according to two different structures is said to exhibit tautomerism (Gk. *tauto*, the same ; *meros*, a part).

Tautomerism is thus a special kind of isomerism, wherein the two isomerides are represented by one and the same substance. According to the one generally accepted view, which was first put forward by Baeyer, a tautomeric substance consists of a mixture of two labile forms in dynamic equilibrium with each other. For this reason, the term **dynamic isomerism** is sometimes used instead of tautomerism. The change of one form of a tautomeric substance into the other is caused by the migration of a hydrogen atom from one polyvalent atom to another, and is accompanied by the necessary rearrangement of linkages. Thus in the case of hydrocyanic acid the change from one form into the other occurs as follows :

$$H-C\equiv N \rightleftharpoons H-N\overset{\rightarrow}{=}C$$

On account of the change of linkage involved in the transformation of one form of a tautomeric substance into the other, the phenomenon is sometimes termed **desmotropism** (Gk. *desmos*, a bond : *tropos*, turn).

Of the many known examples of tautomerism, mention may also be made of the following :

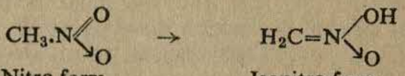
Cyanic acid :

$$HO-C\equiv N \rightleftharpoons O=C=NH$$

Acetoacetic ester :

$$\underset{\text{Keto form}}{CH_3CO.CH_2.COOEt} \rightleftharpoons \underset{\text{Enol form}}{CH_3.C(OH)=CH.COOEt}$$

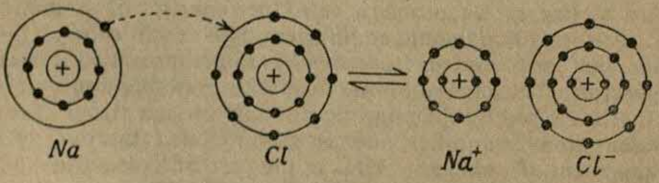
Nitromethane :



Nitro form Isonitro form

15. Electronic Theory of Valency.—When different elements are brought together, their atoms may combine to form compounds. The combining capacity of atoms is termed **valency.** According to modern theory, the development of valency by an atom depends on the number of electrons in the outermost shell, or the "valency shell", of the atom. The key to the nature of valency is provided by the elements of the helium family (zero group of the periodic table). The atoms of these elements possess no power to combine with other atoms, and are, therefore, supposed to possess maximum stability of the valency shell. The helium atom has 2 electrons in the valency shell, while all the other members of this group have 8. Atoms of all elements tend to have a complete shell of 8 electrons (except hydrogen and helium which can have a maximum of 2). It is this tendency of the atom that is responsible for chemical combination. The completion of the valency shell may be achieved by an atom by borrowing, lending or sharing of electrons. The borrowing or lending of electrons gives rise to **electrovalency** (sec. 16), while sharing results in the development of **covalency** (sec. 17).

16. Electrovalency.—Union between atoms may take place by the *transfer* of electrons from the outermost shell of the one to that of the other. Thus, when a chlorine atom having 7 valency electrons combines with a sodium atom having one such electron, the electron from the latter atom is transferred to the chlorine atom. Both the atoms now have a stable arrangement of 8 electrons in the outermost shell. Further, the transfer of an electron from the sodium to the chlorine atom makes the former acquire a unit positive



charge, and the latter a unit negative charge. These charged atoms or *ions* hold each other by an electrostatic force called **electrovalency.**

The change is most conveniently represented as follows :—

$$\dot{\mathrm{Na}} \quad + \quad :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \quad \rightleftharpoons \quad \mathrm{Na}^{+}\ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{-}$$

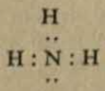
Sodium Chlorine Sodium chloride

A compound formed in this way is termed an **electrovalent compound.**

17. Covalency.—This type of union is especially prevalent among organic compounds. In this case, the atoms undergo combination by *sharing* one, two or three pairs of electrons with each other so as to complete their octets. In each pair of shared electrons one is contributed by each atom. One pair of shared electrons corresponds to a **single bond**, two pairs to a **double bond**, and three pairs to a **triple bond.** The following are some examples of covalent compounds :—

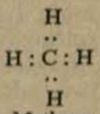
$$\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}$$

Water



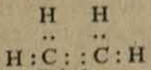
$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}:\mathrm{N}:\mathrm{H}\\ \cdot\cdot\end{array}$$

Ammonia



$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}:\mathrm{C}:\mathrm{H}\\ \cdot\cdot\\ \mathrm{H}\end{array}$$

Methane



$$\begin{array}{c}\mathrm{H}\quad\mathrm{H}\\ \cdot\cdot\quad\cdot\cdot\\ \mathrm{H}:\mathrm{C}::\mathrm{C}:\mathrm{H}\end{array}$$

Ethylene

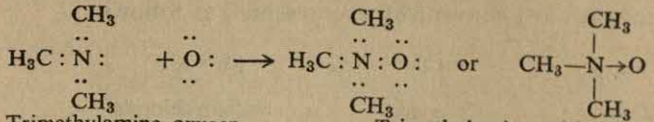
$$\mathrm{H}:\mathrm{C}:::\mathrm{C}:\mathrm{H}$$

Acetylene

18. Co-ordinate Link or Semipolar Bond.—This form of linkage is similar to the covalent link except that *both* the electrons constituting the bond are supplied by *one* of the atoms. Sidgwick calls this a *co-ordinate link*, since he has shown it to exist in Werner's co-ordinate compounds.

A necessary condition for the formation of a co-ordinate link is that one of the atoms, called the **donor**, must have at least one lone pair of valency electrons, *i.e.*, those not concerned in union with any other part of the molecule, while the other atom, called the **acceptor** must require the electrons to complete its octet. Many atoms, even in the state of combination, have one or more lone pairs of electrons. Thus, nitrogen in ammonia has one such pair and oxygen in water has two (though only one of these is regarded as effective). A "covalently saturated" molecule like CH_4 or C_2H_6 cannot provide a donor, since all its valency electrons are shared.

In the formation of a co-ordinate link, the donor retains the number of its valency electrons unchanged, while the acceptor increases its own number by two. A simple example of the formation of a co-ordinate link is that of **trimethylamine oxide.** In trimethylamine, $(CH_3)_3N$, as in ammonia, the nitrogen atom has a lone pair of electrons, while the oxygen atom requires a pair of electrons in order to complete its octet. Hence the change may be represented as follows :—



$$\mathrm{H_3C:\overset{\overset{\Large CH_3}{\cdot\cdot}}{\underset{\underset{\Large CH_3}{\cdot\cdot}}{N}}:} + \mathrm{\ddot{\underset{\cdot\cdot}{O}}:} \longrightarrow \mathrm{H_3C:\overset{\overset{\Large CH_3}{\cdot\cdot}}{\underset{\underset{\Large CH_3}{\cdot\cdot}}{N}}:\ddot{\underset{\cdot\cdot}{O}}:} \quad \text{or} \quad \mathrm{CH_3{-}\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{N}}{\rightarrow}O}$$

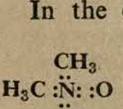
Trimethylamine oxygen Trimethylamine oxide

In the second of the above pair of formulæ of trimethylamine oxide a simple covalency is represented by a single line and a co-ordinate link by a short arrow. The single line of the arrow indicates that the link is formed by the sharing of two electrons and the direction of the arrow shows that both the electrons are provided by the nitrogen atom. This mode of representing a co-ordinate valency is due to Sidgwick.

Lowry, who first proposed the above electronic formula for the amine oxides, is of the opinion that the formation of a link like this necessarily implies that the molecule has developed polarity. The nitrogen atom has acquired a positive charge because of its two electrons getting further away from it than prior to the combination, while the oxygen atom acquires a negative charge, because it has received two additional electrons. Hence, the two parts of the molecule are held together not only by the sharing of a pair of electrons, as in a single covalent bond, but also by their mutual electrical attraction. For this reason, Lowry calls this type of linkage a **semi-polar bond**, and indicates its nature by placing the signs + and — against the donor and the acceptor atoms respectively. Thus, the structure of trimethylamine oxide is represented as shown in the margin.

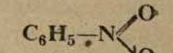
$(CH_3)_3\overset{+}{N}-\overset{-}{O}$

In the older formula of the amine oxides, $R_3N=O$, the presence of a normal double bond was assumed. This is, however, untenable, since if we translate it into the electronic formula we must assume the nitrogen atom to possess a valency group of ten electrons (see margin), which, as we know, is an unstable arrangement. The new formulation is justified by the evidence of Sugden's parachor (chapter 6).

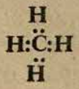


$$\mathrm{H_3C:\overset{\overset{\Large CH_3}{\cdot\cdot}}{\underset{\underset{\Large CH_3}{\cdot\cdot}}{N}}::O}$$

Sugden has shown that most of the double bonds of structural organic chemistry are true double covalent bonds. The nitro group,—NO_2, however, appears to possess one true double bond together with one semi-polar bond, or co-ordinate link. Nitrobenzene, therefore, is assigned the electronic formula given in the margin.



19. Valency of Hydrogen and Oxygen.—The hydrogen atom has only one electron. When this is lost, we get the hydrogen ion, H^+, which is the common constituent of all acids. In organic compounds, hydrogen forms a single covalency, *i.e.*, a 2-electron link, as in methane (see margin).



$$\mathrm{H:\overset{\overset{\Large H}{\cdot\cdot}}{\underset{\underset{\Large H}{\cdot\cdot}}{C}}:H}$$

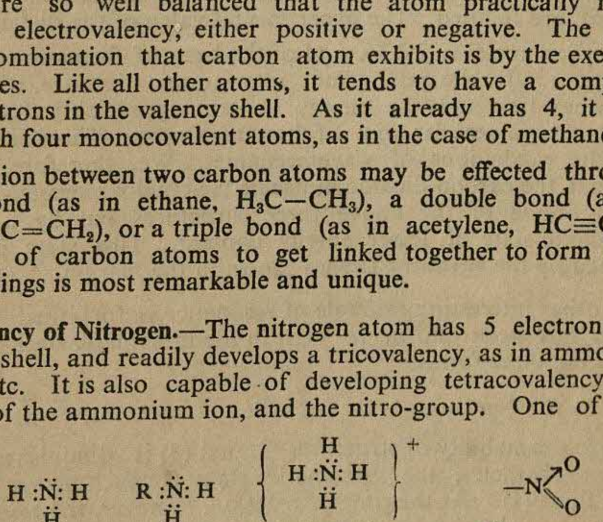
The oxygen atom has six electrons in the valency shell. It may acquire two more from another atom, giving rise to the oxide ion, O^{--}. In the case of organic compounds, oxygen acts as a bicovalent element. In methyl alcohol, $\mathrm{H{:}\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}{:}\ddot{\underset{..}{O}}{:}H}$, for example, oxygen has two single bonds, one with carbon and the other with hydrogen.

The two oxygen atoms of acetic acid, $\mathrm{CH_3.C}{\lessgtr}^{\mathrm{O}}_{\mathrm{OH}}$, are both bicovalent. One of them is bound on the one hand with carbon and on the other with hydrogen, a single covalency being developed in each case. The other oxygen atom is bound to the carbon atom by a double bond, *i.e.*, a 4-electron link. In all these cases, the oxygen atom fills up its valency shell completely. That is, its valency shell acquires 8 electrons, which is the maximum that it can hold.

20. Valency of Carbon.—The carbon atom has 4 electrons in the valency shell, and the opposing tendencies to gain or borrow electrons are so well balanced that the atom practically never develops an electrovalency, either positive or negative. The only mode of combination that carbon atom exhibits is by the exercise of covalencies. Like all other atoms, it tends to have a complete set of 8 electrons in the valency shell. As it already has 4, it will combine with four monocovalent atoms, as in the case of methane.

Combination between two carbon atoms may be effected through a single bond (as in ethane, H_3C-CH_3), a double bond (as in ethylene, $H_2C=CH_2$), or a triple bond (as in acetylene, $HC\equiv CH$). This power of carbon atoms to get linked together to form long chains and rings is most remarkable and unique.

21. Valency of Nitrogen.—The nitrogen atom has 5 electrons in the valency shell, and readily develops a tricovalency, as in ammonia, or amines, etc. It is also capable of developing tetracovalency, as in the case of the ammonium ion, and the nitro-group. One of the nitrogen-oxygen bonds in the latter is normal double bond and the other a co-ordinate link. As the valency shell of the nitrogen atom cannot accommodate more than eight electrons, the maximum covalency of nitrogen, like that of carbon, is four.



$\mathrm{H{:}\overset{..}{\underset{\underset{H}{..}}{N}}{:}H}$ Ammonia $\quad \mathrm{R{:}\overset{..}{\underset{\underset{H}{..}}{N}}{:}H}$ Amine $\quad \left[\mathrm{H{:}\overset{H}{\underset{\underset{H}{..}}{\ddot{N}}}{:}H}\right]^{+}$ Ammonium ion $\quad -\mathrm{N}{\nearrow^{O}_{\searrow O}}$ Nitro-group

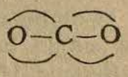
Ammonia Amine Ammonium ion Nitro-group

22. Resonance.—It has been established with the help of wave mechanics that if a molecule can be represented by two (or more different structural formulæ, then its actual state is represented neither by the one formula nor the other, nor yet by a mixture of the two forms as in the case of tautomeric substances; it is in fact a **hybrid structure** intermediate between the two formulæ. The phenomenon is termed *resonance*. The **mesomeric state** of the molecule possesses a minimum of energy, and, therefore, a maximum of stability. For mesomerism to be possible, **two conditions** must be satisfied : First, the position of the atoms in the two structures must be *approximately* the same ; secondly, the energies of formation of the two forms and, therefore, their stabilities must not be much different.

The **carbon dioxide molecule** presents one of the simplest examples of resonance. It may be represented by any of the following three formulæ :—

(1) $O=C=O$ (2) $\overset{-}{O}-C\equiv\overset{+}{O}$ (3) $\overset{+}{O}\equiv C-\overset{-}{O}$

The structures (2) and (3) are derived from (1) by electronic displacement. The distances between the oxygen atoms for the three formulæ, as calculated theoretically, are very nearly identical (about 2·56 angstrom)[1]. The energy of formation of each form is very nearly 350 kilo-cals. Hence the two necessary conditions for resonance, *viz.*, similarity in nuclear positions and in energy content, are fulfilled. The experimental value of the distance between the oxygen nuclei is 2·30 Å and of the heat of formation of carbon dioxide, 380 kilo-cals. The inter-atomic distance, therefore, is somewhat less and the energy content appreciably less than the calculated values for any of the three forms. This is in agreement with the predictions of wavemechanics. We, therefore, see that the carbon dioxide molecule is actually represented by none of the above three structures but by a mesomeric state of lower energy content. This state is generally denoted by the **mesomeric formula** shown in the margin.



Another interesting example of resonance is furnished by **ethylene**, which has been shown to exist in the mesomeric state between the following three forms.

(1) $>C=C=<$ (2) $>\overset{+}{C}-\overset{-}{C}<$ (3) $C>\overset{-}{C}-\overset{+}{C}<$

Since the stability of structures (2) and (3) is diminished by their dipolar character, the mesomeric state is much nearer to the non-polar form (1). At the time of reaction, however, the transformation of the non-polar into one of the polar forms occurs. It is on the basis of this **polar activation of the double bond** that the addition reaction of ethylene and other unsaturated compounds are generally explained.

The phenomenon of resonance is of considerable interest, and has been successfully employed in the elucidation of the behaviour of a number of molecules and groups, such as the nitro-group, the carbonyl group, the carboxylate ion, the azide ion, the benzene ring, etc. The **resonance in benzene ring** is discussed in chap. 34, sec. 12.

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[1] The *Angstrom unit* (denoted by Å) is employed in expressing wave-length of different radiations and distances between atoms in a molecule. It is equal to 10^{-8} cm.

QUESTIONS

1. Give the different steps in the systematic investigation of the formula of an organic compound.

2. Distinguish between *nuclear isomerism*, *position isomerism*, and *metamerism*. Give illustrative examples.

3. Give a brief account of Baeyer's Strain Theory and show how it explains the instability of unsaturated compounds and the increasing stability of cycloparaffins. Can you explain the stability of benzene by means of this theory? (*Punjab, B.Sc., 1950*)

4. Write a short note on 'conjugated double bonds'. (*Punjab, B.Sc., 1925*)

5. Show how the constitution of an organic compound can be determined by its chemical behaviour and synthesis. (*Punjab, B.Sc., Hons., 1926*)

6. Explain, with appropriate examples, Thiele's theory of partial valency as applied to unsaturated organic compounds. (*Punjab, B.Sc., 1960*)

7. "The *valency* of hydrogen, oxygen and chlorine in organic compounds is 1, 2 and 1 respectively." What is the significance of this statement from the viewpoint of modern theory?

8. "While carbon is consistently tetra-covalent, nitrogen may act as a tri-covalent or a tetra-covalent element." Why is it so?

9. Write a note on Resonance.

10. Write a clear and concise note on the fundamental assumptions on which the structural theory is based. (*Rajasthan, B.Sc., 1961*)

11. Write a short note on Tautomerism. (*Lucknow, B.Sc., 1959*)

12. Discuss Baeyer's strain theory and its applications. State its limitations. How has it been modified to explain large membered rings? (*Bombay, B.Sc., 1954*)

CHAPTER SIX

RELATION BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

1. General.—The study of certain physical properties has proved very helpful in elucidation of the constitution of some organic substances. An attempt is first made to establish the relationship that exists between a given physical property and the structure of the molecule in compounds of known constitution. The relationship thus deduced is then made use of in deciding between two or more alternative constitutions that could be assigned to the compound under investigation.

Classification of Physical Properties.—

From the point of view of our present study, physical properties may be divided into three distinct classes :—

(1) **Additive Properties.** These depend on the number and kind of atoms present in the molecule. A well-known example of a purely additive property is that of *molecular weight*, which is exactly equal to the sum of the masses of the component atoms.

(2) **Constitutive Properties.** These depend on the constitution of the molecule, *i.e.*, on the arrangement of atoms within the molecule. Thus, the *optical rotation* of polarized light depends only on the presence of an "asymmetric" carbon atom, *i.e.*, one linked to four different atoms or groups.

(3) **Colligative Properties.** These depend only on the *number* of atoms or molecules present. The gas pressure and the osmotic pressure of a solution are typical examples of colligative properties.

Most of the physical properties, however, are **partly additive and partly constitutive.** Molecular refraction, parachor and atomic volume are examples of this type.

A study of certain physical properties of organic substances has been found very helpful for the elucidation of the structure of the molecule. The determination of the more important of such physical properties and their application in the study of chemical constitution are given below.

2. Parachor.—The determination of *"parachor"*, a molecular constant introduced by Sugden in 1924, has proved very useful in solving constitutional problems of controversial nature. The constant is defined by the **parachor equation,**

$$[P]=\left(\frac{M}{D}\right)\gamma^{\frac{1}{4}}$$

where M/D is the molecular volume and γ the surface tension.

It should be noted that **parachor is independent of temperature.** For compounds of similar structure (as is the case with members of a given homologous series of organic compounds) the molar parachor is equal to the sum of the gram-atomic parachors. Where there is a difference of molecular structure, however, there is a corresponding change in the value of parachor. Thus, parachor is a property that **is partly additive and partly constitutive.**

Molar Parachors.—

In the determination of molar parachors we first determine the density and surface tension, both at the same temperature. By substituting these values and of the molecular weight in the parachor equation, we obtain the value of **molar parachor** for the compound under examination.

Example 1. *p-chlorotoluene has a density of 1·065 gm. per ml. at 25°C and its surface tension at that temperature is 32·24 dynes per cm. Calculate the value of its molar parachor.*

The molecular weight of *p*-chlorotoluene, $C_6H_4(CH_3)Cl$,

$$M=72+4+15+35{\cdot}5=126{\cdot}5.$$

Substituting the values of *M*, *D* and γ in the parachor equation

$$[P]=\frac{M}{D}\ \gamma^{\frac{1}{4}}$$

we get the molar parachor of *p*-chlorotoluene :

$$[P]=\frac{126{\cdot}5}{1{\cdot}065}\times(32{\cdot}24)^{\frac{1}{4}}=\mathbf{283.}$$

Example 2. *Benzene, C_6H_6, has a density of 0·879 gm./ml. at 20°C and its surface tension at that temperature is 28·9 dynes per cm. Find the value of its molar parachor.*

The molecular weight of benzene, C_6H_6,

$$M=72+6=78$$

Inserting the values of *M*, *D* and γ in the parachor equation, we get

$$[P]=\frac{78}{0{\cdot}879}\times 28{\cdot}9^{\frac{1}{4}}=\mathbf{206.}$$

The molar parachor has been shown to be an additive property of a simple type, and is made up of two series of constants, one for the atoms and the other for the linkages present in the molecule. For isomeric substances, whose constitutions differ only in the position of groups or linkages in the molecule, the parachors are found to be identical. The following examples illustrate this fact :—

PARACHORS OF SOME ISOMERIC ESTERS

Methyl valerate	292·5
Ethyl butyrate	293·6
n-Propyl propionate	295·3
i-Butyl acetate	295·1
i-Amyl formate	293·6

PARACHORS OF ISOMERIC XYLENES

o-Xylene	283·3
m-Xylene	283·8
p-Xylene	283·8

Atomic Parachors.—

Sugden, by comparing the parachor values for successive members of a homologous series, calculated a mean constant difference for CH_2. For instance, the observed parachors for ethane, C_2H_6, and decane $C_{10}H_{22}$, are respectively 111·0 and 424·2. Hence, the mean value for CH_2 is $\frac{424{\cdot}2-111{\cdot}0}{8}$ or 39·0. From this the parachors for carbon and hydrogen can be calculated as follows :—

Parachor for decane, $C_{10}H_{22}=424{\cdot}2$
Parachor value $10\times CH_2=390{\cdot}0$
$\therefore$ Parachor for $2H=34{\cdot}2$
,, ,, $H=17{\cdot}1$
,, ,, $C=39{\cdot}0-34{\cdot}2=4{\cdot}8$

Similarly, the parachor values for other elements can be calculated from the parachors of saturated aliphatic compounds.

Structural Parachors.—

In all saturated compounds, the **parachor of the single covalent bond is arbitrarily taken as zero.** If we compare the parachors of saturated, open-chain hydro-carbons with those of unsaturated and cyclic types, we find that a definite contribution is made by each double bond, triple bond, and 3-, 4-, 5-, or 6 membered ring that the molecule may contain. Some of the atomic and structural parachors thus deduced are tabulated below :—

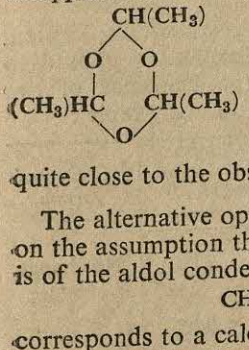
Atomic parachors		*Structural parachors*	
C	4·8	Double bond	23·2
H	17·1	Triple bond	46·6
O	20·0	3-membered ring	16·7
N	12·5	4- ,, ,,	11·6
S	48·2	5- ,, ,,	8·5
P	37·7	6- ,, ,,	6·1
Cl	54·3	Semi-polar double bond	1·6
Br	68·0	O_2 in esters	60·0

It has been found that the **parachor value for the double bond is independent of the nature of the atoms linked**, and is the same for the links C=C, C=O, C=S, C=N, N=O. Similarly, the value for the triple bond in nitriles and acetylene and its derivatives is the same, *viz.*, 46·6, which is almost exactly twice the value for a double bond. Hence it is not possible to distinguish between compounds such as $CH_3O{\cdot}C{\equiv}N$ and $CH_3N{=}C{=}O$ by a parachor determination.

3. **Applications of Parachor.**—Parachor has been useful in the field of molecular structure in two ways :—

(A) IN DECIDING BETWEEN ALTERNATIVE CONSTITUTIONS. Some noteworthy examples are :—

(1) **Structure of Paraldehyde.** When acetaldehyde, CH_3CHO, is treated with a trace of concentrated sulphuric acid, it changes to a trimer, $(C_2H_4O)_3$. As the parachor of acetaldehyde is 121·2, three molecules would correspond to a parachor of 363.6. But the parachor of paraldehyde is only 298·7, *i.e.*, about 65 units less. On looking up the table of structural parachors, we see that the parachor for the double bond is 23·2. Three double bonds, present is the three molecules of acetaldehyde that have undergone polymerization, correspond to a parachor equal to about 70. So, it appears that in the formation of paracetaldehyde, the *three double bonds have disappeared.* Hence, paraldehyde should be assigned a structure having no double bonds. The generally accepted formula for paraldehyde (given in the margin) consists of a six-membered ring containing 3 oxygen and 3 carbon atoms with no double bonds, and corresponds to a calculated parachor of about 300, which is quite close to the observed value.



The alternative open-chain formula, that might have been assigned on the assumption that the conversion of acetaldehyde to paraldehyde is of the aldol condensation type, *i.e.*,

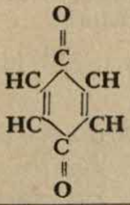
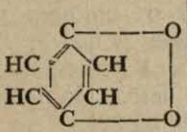
$$CH_3.CH(OH).CH_2.CH(OH),CH_2.CHO,$$

corresponds to a calculated parachor value of 317·2, which is much higher than the observed value of 298·7.

(2) **Benzene.** The parachor determination of benzene and a large number of its derivatives shows that the molecule contains three normal double bonds as formulated by Kekule. Thus, the value for benzene is found to be 206·2, and as calculated theoretically it should be 207·1.

6C	6× 4·8= 28·8
6H	6×17·1=102·6
3 double bonds	3×23·2= 69·6
6-membered ring	= 6·1
	Total =207·1

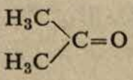
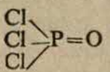
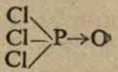
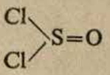
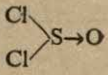
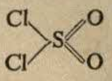
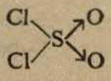
(3) **Quinone.** The two structural formulae proposed for quinone and the corresponding calculated parachor values are given below :

Formula	*Calculated Parachor*	
	6C	6× 4·8= 28·8
	4H	4×17·1= 68·4
	2O	2×20·0= 40·0
	4 double bonds	4×23·2= 92·8
	1 six membered ring	6·1= 6·1
		Total =236‘1
	6C	6× 4·8= 28·8
	4H	4×17·1= 68·4
	2O	2×20·0= 40·0
	3 double bonds	3×23·2= 69·6
	2 six membered rings	2× 6·1= 12·2
		Total =219·0

The observed parachor value of quinone is 236·8, which clearly shows that the first formula for the compound is the correct one.

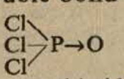
(B) IN DECIDING THE NATURE OF CERTAIN VALENCY BONDS :—

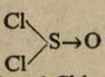
(1) **Semipolar Double Bond or Co-ordinate Link.** A study, by Sugden, of the parachor values of compounds that were formerly supposed to contain one or more double bonds revealed the existence of *two* kinds of double bonds, as will appear from the following table :—

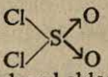
Compound	*Old formula*	*Observed parachor*	*Calculated value*	*Difference due to double bond*	*Corrected formula*
Ethylene	$H_2C=CH_2$	99·5	78·0	21·5	No change
Acetone		161·5	137·0	24·5	”
Nitrosyl chloride	Cl—N=O	108·1	86·8	21·3	”
Phosphorus oxychloride		217·6	220·6	−3·0	
Thicny chloride		174·5	176·8	−2·3	
Sulphuryl chloride		193·3	196·8	−1·65×2	

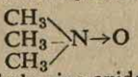
Majority of unsaturated compounds, *e.g.*, ethylene and ethlenic compounds in general, give for the double bond an average parachor value of +23. It always possesses practically the same value irrespective of the nature of atoms between which it occurs.

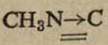
The other class of compounds formerly supposed to have the presence of a double bond in the molecule, though in minority, stood prominently apart with a small *negative* parachor value of about −2 units. On attempting to write the electronic formulae of these latter compounds, using a double covalent linkage, it was found that this could only be done by breaking the octet rule and assigning to one of the atoms taking part in the double bond a valency group of 10 or more electrons. In all such cases, it is possible to preserve the octet rule by writing the double linking as a semi-polar double bond or a co-ordinate covalency. Examples of compounds containing semi-polar double bond are :

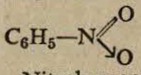

Phosphorus oxychloride


Thinoyl Chloride

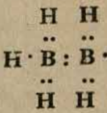

Sulphuryl chloride


Trimethylamine oxide

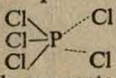

Methyl isocyanide

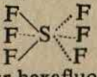

Nitrobenzene

(2) **Singlet Linkage.** Though in most cases a single covalent link is constituted by the sharing of a *pair* of electrons, there are a few cases where a *single* shared electron constitutes the link. This is termed a *singlet* or a *singlet linkage.* The most indisputable evidence for the existence of a singlet is furnished by the **hydrogen molecule ion**, $[H_2]^+$, which is found to occur in positive ray discharge tubes. This must be assigned the structure $[H.H]^+$. Another important class of compounds definitely containing singlets are the hydrides of boron ; *e.g.*, **boroethane** (*see* formula in the margin).



The evidence for the existence of the singlet is fully supported by the parachor values of **phosphorus pentachloride** and **sulphur hexafluoride.** The formulae of these compounds together with observed and calculated values of parachor are given below :


Phosphorus pentachloride
[P] (calculated) = 284·4
[P] (observed) = 282·5


Sulphur hexafluoride
[P] (calculated) = 148·6
[P] (observed) = 143·3

In the above formula a normal single bond is indicated, as usual, by a single line and the singlet by a dotted line.

The parachor value of the singlet, used in the calculation, is deduced as follows :

[P] for a triple bond (consisting of 6 electrons) = 46·6
[P] for a double bond (consisting of 4 electrons) = 23·3
[P] for a single bond (consisting of 2 electrons) = 0
∴ [P] for a singlet (consisting of 1 electron) = −11·6

4. Optical Activity.—The property possessed by certain substances of rotating the plane of polarization of light is termed optical activity. To understand the **phenomenon of polarization**, we may take the following mechanical illustration : Suppose we have a tightly stretched string knotted near the middle. The knot is free to move in any direction at right angles to the string. Hence, if we pluck the string, the knot will be found, in all probability, to describe a series of figures varying between a circle and a straight line. Every point on the string will, of course, be vibrating in a similar manner. Now, suppose that we take a card in which a slit has been cut, slip it on to the string near the knot, and pluck the string once again. This time the knot will be found to vibrate only in one direction namely the direction of the slit. Suppose that we now take another piece of card with a slit cut in it, and slip it on to the string near the first card. We shall then see that the knot can vibrate only when the slits lie parallel to each other ; if the two slits lie at an angle, the string is gripped, and is not able to vibrate at all at that point.

Polarization of Light.—

According to the modern theory, a ray of light is propagated through space as vibrations in ether, which take place in all directions perpendicular to the line of propagation of the ray (Fig. 1). If the ray be passed through a Nicol prism, cut in a certain manner from a crystal of Iceland spar, the vibrations get restricted and take place only in one direction. We say that the light has been *polarized*. In Fig. 1A, a beam, *L*, of ordinary light is shown to be passing in a direction perpendicular to the plane of the paper, the vibrations in ether taking place in all the directions, *aa*, *bb*, *cc*, etc. Fig. 1B shows a beam, *L'*, of polarized light, in which the vibrations take place only in one direction, *viz.*, *aa*. A plane drawn through the direction of polarized ray, and perpendicular to the direction in which the ether vibrations occur, is called the **plane of polarization**. In Fig. 1 the plane of polarization cuts the plane of the paper along the line *PP*.

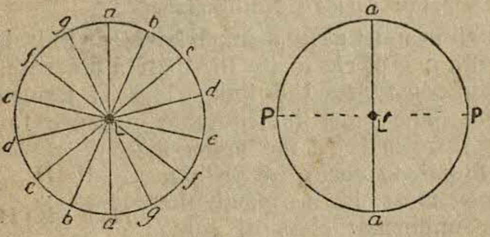


Fig. 1.

A (ordinary light) B (polarized light)

If the polarized ray be passed through a second Nicol prism placed with its plane of polarization parallel to that of the first, the ray will pass through it as it did through the first one. If we rotate the second prism, the quantity of light passing through will continuously diminish, until when the prism has been rotated through an angle of 90°, the light has been entirely cut off. In other words, the position of *maximum brightness* is followed at an interval of 90° by a position of *maximum darkness*, at an interval of 180° by a second position of maximum brightness, and at an interval of 270° by a second position of maximum darkness. The first Nicol prism, which causes polarization of light, is called the **polarizer**, while the second one, through which the polarized light is examined, is called the **analyser.**

If, when the polarizer and the analyser are in the position of maximum darkness, we place between them a tube containing a solution of cane-sugar, the field of view will be found to have become more or less bright, showing that the plane of polarization of light falling on the analyser has been rotated by the cane-sugar solution. If now we slowly rotate the analyser towards the right, *i.e.*, clockwise, the position of maximum darkness will once again be reached. The angle through which the analyser has to be turned, in order to attain the position of maximum darkness once again, measures the degree of rotation of the plane of polarization by the cane-sugar solution.

Cane-sugar and other substances that have the power to rotate the plane of polarization in the above manner are said to be **optically active.** If, as in the case of cane-sugar, the analyser is to be turned towards the right (*i.e.*, clockwise) to re-attain the position of maximum darkness, the substance is said to be **dextrorotatory** ; if, on the other hand, it is to be turned towards the left (anti-clockwise) the substance is called **laevorotatory.**

Polarimeter.—

The simple arrangement of two Nicol prisms described above does not give accurate results. The reason is that the analyser, when arranged in the position of maximum darkness, can be turned through a small angle in either direction without allowing any light to pass through. Various types of polarimeters have been designed to overcome this difficulty. One of those in common use is the **Laurent half-shadow polarimeter** shown in Fig. 2.

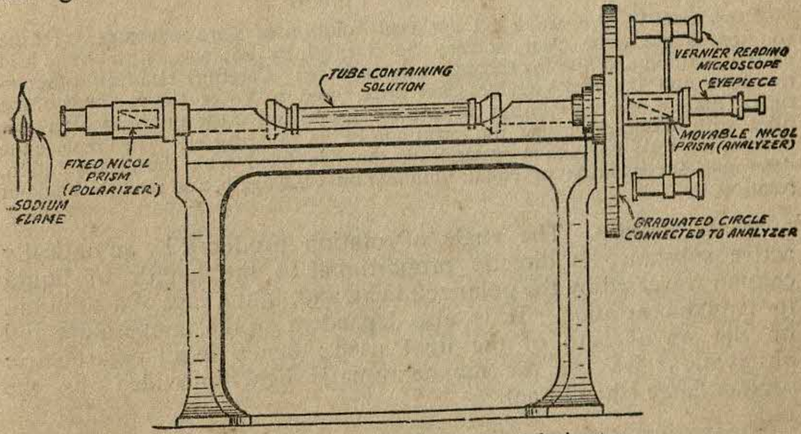

TUBE CONTAINING SOLUTION
VERNIER READING MICROSCOPE
EYEPIECE
MOVABLE NICOL PRISM (ANALYZER)
FIXED NICOL PRISM (POLARIZER)
SODIUM FLAME
GRADUATED CIRCLE CONNECTED TO ANALYZER

Fig. 2. Laurent's Half-shadow Polarimeter.

The arrangement of the optical parts of this instrument is shown in Fig 3. Monochromatic light from a **sodium lamp**, *S*, is passed

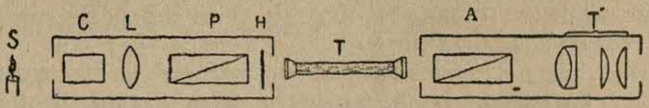


Fig. 3. Optical parts of the Half-shadow Polarimeter.

through a cell, *C*, containing 6 per cent potassium dichromate solution, which serves to absorb the blue or violet rays. Next it passes through the **collimating lens**, *L*, which serves to render the rays parallel, and then through the **polarizer**, *P*. The polarized light passes through the half-shade, *H* (see below), and then through the liquid under examination contained in the observation tube, *T*. After traversing the liquid, the polarized light passes through the **analyser**, *A*, and finally emerges from the instrument through the eye-piece of the telescope, *T′*. The analyser may be rotated through any desired angle, and the amount of rotation measured on a graduated scale.

The **half-shade**, *H*, serves to determine exactly the point of maximum darkness. It consists of a combination of semi-circular plates of glass and quartz. Over a certain range of the scale, the right-hand half of the field is darker than the left ; beyond this range the left-hand half gets darker than the right-hand half. The intermediate position where the illumination is uniform on the two sides of the field is taken as the zero point.

Experiment 1. Prepare a 50 per cent solution of pure cane-sugar. (If the solution is not quite clear, it may be clarified by adding a little basic lead acetate solution and filtering through a fluted filter.) Carefully clean an observation-tube and the two circular glass discs, used to cover the two ends of the tube. Fix up the polarimeter in a dark room, and using an observation tube filled with water determine the zero point of the polarimeter. Then replace the observation-tube containing water with the one filled with the sugar solution, determine the position of equal illumination once again, and read the angle of rotation.

Specific Rotation. The angle of rotation produced by an optically active substance is directly proportional to the length of liquid column traversed by the polarized light, and, in the case of a solution, to its concentration. It is also dependent on the temperature and on the wave-length of the light used ; hence in all polarimetric observations we use the monochromatic light provided by the sodium flame (the D line).

The optical activity of a substance is usually expressed as its **specific rotation** $[\alpha]^t_D$, the value of which, in the case of a liquid, is given by the expression

$$[\alpha]^t_D = \frac{\alpha}{l \times d}$$

where α is the observed angle of rotation, t the temperature in degrees centigrade, l the length in decimetres of the liquid column in the observation tube, and d the density of the optically active liquid at the temperature of the experiment. The fact that sodium light has been used in the experiment is indicated by the letter D.

In the case of a solution of an optically active substance in water, or some other optically inactive solvent, the above expression becomes

$$[\alpha]_{\mathrm{D}}^{t} = \frac{\alpha}{l} \times \frac{v}{w}$$

where w is the weight of the substance in grams present in v ml. of the solution.

The specific rotations, at 20°, of a few optically active substances are listed in the table given in the margin :—

Substance	$\left[a\right]_{\mathrm{D}}^{20}$
Cane-sugar	+66·5°
Glucose	+52·5
Fructose	−92

For comparing the optical activities of different substances we employ the term **molecular rotation.** This is denoted by $[M]_{\mathrm{D}}^{t}$ and is obtained by multiplying the specific rotation of a substance by its molecular weight and dividing by 100 in order to avoid unwieldy numbers :

$$[M]_{\mathrm{D}}^{t} = \frac{[a]_{\mathrm{D}}^{t}\ M}{100}.$$

Optical Activity and Molecular Structure.—

The relationship between optical activity and the structure of the molecule is discussed in the chapter on Stereochemistry.

5. Magnetic Rotation.—A beam of polarized light, when passed through a transparent substance in the direction of the lines of force of a strong magnetic field, undergoes rotation. This property of **magnetic rotation** is shown by *all* transparent substances, and should be distinguished from optical activity, which is possessed only by substances containing an asymmetric carbon atom. For the sake of comparison, magnetic rotation of different substances is expressed as **molecular magnetic rotation**, which may be defined as the *rates of he expression RM/D for the substance to the corresponding value for water*, where R is the rotation due to a column of given length of the substance in a magnetic field of given strength, M the molecular weight of the substance and D its density. Hence, if the rotation for a column of the same length of water in a magnetic field of the same strength be r, m the molecular weight of water and d its density, then the molecular magnetic rotation RM, is given by the following equation :—

$$RM = \frac{RM/D}{rm/d.} = \frac{RMd}{rmD}.$$

The application of molecular magnetic rotation to the study of chemical constitution was first made by Sir W. H. Perkin, who found that the property is *additive* as well as *constitutive.* It is additive in that there is constant increment for each CH_2 group in the various homologous series ; it is constitutive in that for each homologous series there is a different **series constant**, *h*. The value for CH_2 was found by Perkin to be 1·023. The molecular magnetic rotation of a substance containing *n* carbon atoms is given by the equation—

$$RM = h + 1{\cdot}023\, n,$$

h being the constant for the homologous series to which the substance belongs.

The values of *h* for some of the homologous series are :—

normal-paraffins	0·508	*iso*-acids	0·509
normal-alcohols	0·699	*ketones*	0·375
iso-alcohols	0·844	*diketones*	0·372
normal-acids	0·303		

The determination of molecular magnetic rotation has been used by Perkin in the study of keto-enol tautomerism and of terpenes. The value for **ethyl acetoacetate** was found by Perkin to be 6·501, whence he concluded (see Example 3 below) that the ester possessed the *ketonic* structure. Later work, however, has shown conclusively that the ester contains an appreciable proportion of the enolic form.

Example 3. *Perkin found the molecular magnetic rotation of ethyl acetoacetate,* $CH_3.CO.CH_2.CO.OC_2H_5$, *to be 6·501 and of ethyl lactate,* $CH_3.CHOH\ CO.OC_2H_5$, *5·714. Given that—*

(*i*) *the value for* CH_2 *is 1·023,*

(*ii*) *the series constant for a diketone is 0·372,*

(*iii*) *the increment for the conversion of saturated into the corresponding unsaturated ester (by removing two hydrogen atoms and introducing a double bond) is 1·112.*

what conclusion would you draw as to the structure of ethyl acetoacetate ?

Ethyl acetoacetate may possses the ketonic structure, $CH_3CO.CH_2.CO.OC_2H_5$, or the enolic structure, $CH_3C(OH){=}CH.CO.OC_2H_5$.

The molecular magnetic rotation of the *keto*-form should be

$$= 0{\cdot}372 + 6 \times 1{\cdot}023 = 6{\cdot}510.$$

The value for the enolic form may be calculated from that of ethyl lactate, which contains one carbon atom less than ethyl acetoacetate. The molecular magnetic rotation of ethyl hydroxy-butyrate, the next homologue of ethyl acetoacetate, should be

$$= 5{\cdot}714 + 1{\cdot}023 = 6{\cdot}737.$$

Adding to this figure, 1·112, the increment for the conversion of a saturated into the corresponding unsaturated ester, we get the value 7·849 for the *enolic* form of acetoacetic ester.

Hence we see that the observed value of molecular magnetic rotation for ethyl acetoacetate, 6·501, is within experimental error, identical with that calculated for the *keto* form and very much lower than that calculated for the enol form. The ester must, therefore, be assumed to possess the **ketonic structure.**

6. Molecular Refraction and Chemical Constitution.—The refractive index of a fluid varies with temperature and pressure, as these factors alter the number of molecules in the path of the light. Hence, it cannot be used to compare refractive powers of different fluids in relation to their molecular structures.

To eliminate the effect of these factors, H. A. Lorentz (1880) from the electromagnetic theory of light, and L. V. Lorenz (1880), from the wave theory of light, independently deduced the following theoretical relationship between refractive index and density, which should be constant at all temperatures :—

$$\frac{n^2-1}{n^2+2}\times\frac{1}{d}=R$$

The constant R is termed the **specific refraction,** n is the refractive index and d the density of the liquid.

In order to compare the refractive powers of different substances, their specific refractions are multiplied by their respective molecular weights. The product is termed **molecular refraction,** and is defined by the equation :

$$R_m=\frac{n^2-1}{n^2+1}\times\frac{M}{d}$$

where R_m is the molecular refraction, M the molecular weight, n the refractive index and d the density.

The molar refraction is independent of temperature and pressure, but, as is the case with refractive index, it varies with the wavelength of the light used. Generally, the D-line of sodium is the light source. If any other source is employed (*e.g.*, the α-line in the hydrogen spectrum) it should be specifically mentioned.

The **molar refractions** of some common liquids for D-line are tabulated below :—

C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	CH_3COCH_3
12·78	12·93	22·25	16·15
CCl_4	C_6H_6	$C_6H_5CH_3$	H_2O
26·51	26·18	30·92	3·75
$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_5CH_3$	$CH_3CH_2CH_2OH$	$CHCl_3$
29·908	34·519	17·398	21·25

Molar Refraction as an Additive and Constitutive Property.—

Molar refraction is mainly an *additive* property, and may be determined by adding up the **refraction equivalents** of atoms and structural units. The refraction values of atoms are more commonly called **atomic refractions.**

Molar refraction is also *partly constitutive*, depending on the nature of linkages present.

The additive nature of molar refraction is borne out by the facts—

(1) *Similarly constituted isomers possess practically the same molar refraction.*

For example, the molar refractions, for α-line of hydrogen spectrum, of *n*-propyl alcohol, $CH_3(CH_2)_2OH$, and isopropyl alcohol, $(CH_3)_2CHOH$, are 17·44 and 17·42 respectively.

(2) *The difference between the molar refractions of successive members of a homologous series, i.e.,* the **value for the CH_2 group,** *is practically constant.* As an illustration, we may give the molar refractions (for *D*-line of sodium spectrum) of a few alkanes :—

Alkane	$[R_m]_D$	*Value for CH_2*
Hexane	29·878	...
Heptane	34·496	4·618
Octane	39·100	4·604
Nonane	43·716	4·616

The average increment of $[R_m]_D$ for the CH_2 group, however, varies from 4·606 in a series of esters to 4·634 in the series of alcohols. The value **4·618** generally adopted is a *mean* figure for calculating the atomic refractions of hydrogen and carbon. So, there may be an error of as much as 0·016 in these values.

The **dependence of molecular refraction on constitution** of the molecule is illustrated by the fact that the atomic refractions for oxygen differ from one another in alcohols, ethers and ketones (see the Table given on the next page). *It is this difference that is utilized in solving constitutional problems.*

Method of calculation. The method adopted for the calculation of atomic and structural refractions is illustrated in the following example.

Example 4. *From the following values of molar refractions (for D-line of sodium) calculate the atomic and constitutive refractions of (i) CH_2 group, (ii) H, (iii) C, (iv) Br, and (v) C=C.*

Hexane, 29·908 *Heptane, 34·526*
Ethyl brombide, 19·201 *BrH_2C-CH_2Br, 26·966*
$BrHC=CHBr$, 26·500

(*i*) **CH_2 group :—**

$$= R_m \text{ of } n\text{-heptane} - R_m \text{ of } n\text{-hexane}$$
$$= 34{\cdot}526 - 29{\cdot}908 = \mathbf{4{\cdot}618}$$

(*ii*) $$2H = R_m \text{ of } n\text{-hexane, } C_6H_{14} - R_m \text{ of } CH_2 \times 6$$
$$= 29{\cdot}908 - (6 \times 4{\cdot}618) = 2{\cdot}200$$
$$\therefore\ H = \mathbf{1{\cdot}100}$$

(*iii*) $$C = CH_2 - 2H = 4{\cdot}618 - 2{\cdot}200 = \mathbf{2{\cdot}418}$$

(*iv*) $$\mathbf{Br} = C_2H_5Br - 2C - 5H$$
$$= 19{\cdot}201 - 4{\cdot}836 - 5{\cdot}500 = \mathbf{8{\cdot}865}$$

(*v*) $$C{=}C = BrHC{=}CHBr + 2H - BrH_2C{-}CH_2Br$$
$$= (26{\cdot}500 + 2{\cdot}200 - 26{\cdot}966) = \mathbf{1{\cdot}734}.$$

By following the method illustrated in the above example, **refraction equivalents of various atoms and structural units** have been calculated. The values recorded in the table[1] on the opposite page are due to **F. Eisenlohr** (1910). The refraction equivalent is denoted by [R] to which a suffix is added to indicate the spectral line to which the values refer. The suffix D stands for sodium D-line, and α, β and γ refer to α-, β- or γ-lines of the hydrogen spectrum.

---

[1] Slightly different values were obtained by W. Swietoslawski (1920).

Structural unit	$[R]_D$	$[R]_\alpha$	$[R]_\beta$	$[R]_\gamma$
CH_2	4·618	4·597	4·668	4·712
H	1·110	1·092	1·115	1·122
C	2·418	2·413	2·438	2·466
C=C	1·733	1·686	1·824	1 893
C≡C	2·398	2·328	2·506	2·538
O (in CO)	2·211	2·189	2·247	2·267
O (in ethers)	1·643	1·639	1·649	1·662
O (in OH)	1·525	1·522	1·53	1·541
Cl	5·967	5·933	6·043	6·101
Br	8·865	8·803	8·999	9·152
I	13·900	13 757	14·224	14·521

Refraction Equivalents for Nitrogen and Sulphur.—

These have also been determined. However, they are of no fundamental significance, as the values are different for every form of combination. Thus, as many as thirty different refraction equivalents for nitrogen have been calculated by Eisenlohr.

The following values for D-line of sodium, that are of some importance, may be given.

N (in primary amines) ...	2·322
N (in secondary amines) ...	2·499
N (in tertiary amines) ...	2·840
−C≡N	5·459

Use of Atomic Refractions for calculating Molar Refractions.—

The atomic refractions may be used for the calculation of molar refractions of various compounds, and thus checking up the experimental values.

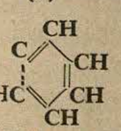
Use of Atomic Refractions for solving Constitutional Problems.—

We may elucidate their use by the following examples :—

(1) **Benzene.** The observed molar refraction of benzene, with respect to α-line in the hydrogen spectrum, is 25·936. According to **Kekule's formula**, there are three double bonds in the molecule. From the table, given above, we find that the appropriate refraction equivalents are :

$$C = 2{\cdot}413\ ;\ H = 1{\cdot}092\ ;\ C{=}C = 1{\cdot}686$$

The calculated value for molar refraction of benzene, therefore, is :—



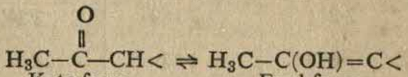
Kekule's formula of benzene.

$$\begin{aligned} 6C &= 2{\cdot}413\times6 = 14{\cdot}478\\ 6H &= 1{\cdot}092\times6 = \ \ 6{\cdot}552\\ \text{3 double bonds} &= 1{\cdot}686\times3 = \ \ \underline{5{\cdot}058}\\ \text{Total} &= 26{\cdot}088 \end{aligned}$$

Hence, we see that the observed value is in fair agreement with the calculated value and fully supports Kekule's formula.

The method has been helpful in clearing up the constitution of several organic compounds, *e.g.*, **thujone, isopinone, α and β terpinenes, and camphene.**

(2) **Keto-enol Tautomerism.** The refractivity determination has been employed for the study of the keto-enol type of dynamic isomerism:



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH< \rightleftharpoons H_3C-C(OH)=C<$$

Keto form Enol form

We see that the change from the keto to the enol form involves the creation of an ethylenic bond and a change from $>C=O$ to $\gt C-O-$. The former means an increase of 1·836 units and the latter a decrease of 2·328−1·505 or 0·822. The change is therefore accompanied by a net increase of 1·014 units Hence, if the molecular refractivity is found to be about 1 unit higher than the theoretical value for the keto form, we infer the presence of a preponderating amount of the enol form. Thus in the case of **acetoacetic ester** the observed molecular refraction for the α-line of hydrogen is found to be 31·89. The values calculated for the ketonic and enolic formulae are respectively 31·5 and 32·5.

Ketonic Form		*Enolic Form*	
$CH_3.CO.CH_2.CO.OC_2H_5$		$CH_3.C(OH)=CH.CO.O.C_2H_5$	
6C	=14·2	6C	=14·2
10H	=11·0	10H	=11·0
2O (carbonyl)	= 4·6	1 ethylene bond	= 1·8
1O (ether)	= 1·7	1O (carbonyl)	= 2·3
Total	31·5	1O (ether)	= 1·7
		1O (hydroxyl)	= 1·5
		Total	32·5

It thus follows that ethyl acetoacetate at the ordinary temperature **consists mainly of the keto form** with a small proportion of the enol form.

7. Anomalous Behaviour of Compounds containing Conjugated Double Bonds.—In certain cases of compounds containing conjugated double bonds, molar refractions are appreciably different from the calculated values. This anomalous behaviour is called **opticol anamaly.** If the observed value is *higher*, as is generally the case, the behaviour is termed **optical exaltation.** The following cases may be clearly differentiated :

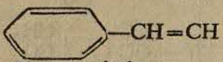
(1) In the case of an *open-chain* compound containing conjugated double bonds, optical exaltation is generally well marked. Thus, we have :—

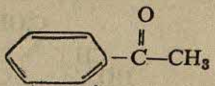
Compound	*Formula*	*Rml*$_D$
2,4-Hexadiene	$CH_3-CH=CH-CH=CH-CH_3$	36·83
1,5-Hexadiene	$H_2C=CH-CH_2-CH_2-CH=CH_2$	34·95

The calculated value is 35·074. Hence, in the case of the first isomer, which contains two *conjugated* double bonds, the value is 1·76 units *higher*, while in the second, in which the double bonds are *non-conjugated*, it is 0·12 unit *lower* than the calculated value.

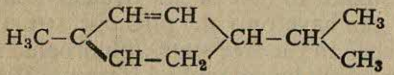
(2) If, however, the conjugated double bonds form a *closed ring* (as, for example, in the case of benzene), there exists no optical anomaly.

(3) If the conjugated system is partly within and partly outside a ring, as in the following cases,


Phenyl-ethylene


Acetophenone

optical exaltation is present. The same is true if there is a gap in the ring, as in the case of α-phellandrene,



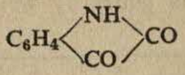
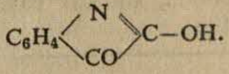
$$H_3C-C\begin{cases}CH=CH\\CH-CH_2\end{cases}CH-CH\begin{cases}CH_3\\CH_3\end{cases}$$

(4) Naphthalene, anthracene and other polynuclear systems possess well marked optical exaltation.

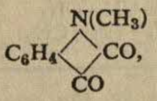
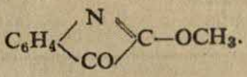
(5) Cyclopropane, cyclobutane and their derivatives also exhibit optical exaltation.

7. Absorption Spectra.—If a beam of ordinary light is allowed to pass through a solution of a coloured substance, a part of the light is absorbed, and dark **absorption bands** appear in the spectrum. Further, it is found that the absorption is not confined to the visible part of the spectrum; it extends to the ultra-violet and the infra-red regions. As yet, little is known of the relation of the infra-red absorption to chemical constitution, while the absorption in the visible and ultra-violet regions has been helpful in the elucidation of the structure of a number of compounds. The absorption in the visible and the ultra-violet regions can be detected by means of photographic plates. Hartley and other investigators have shown that, as a rule, substances of similar constitution give similar absorption spectra.

One of the most important examples of compounds whose structure has been elucidated with the help of absorption spectra is that of **isatin**, which, according to its chemical behaviour, may be either

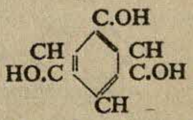
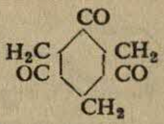
(*i*)  or (*ii*) 

Now, there exist two methyl derivatives of isatin. One of these has been shown to have the constitution

 and the other 

Hartley and Dobbie, in 1899, compared the absorption spectra of these two compounds with that of isatin, and found that the latter was closely similar to that of the *N*-methyl derivative and was quite different from that of the other isomer. Hence, it was concluded that isatin must have the constitution represented by formula (*i*) given above.

Another interesting case is that of **phloroglucinol** which according to its chemical behaviour may be either

(*i*)  or (*ii*) 

Hartley, Dobbie and Lauder found that the absorption spectrum of the compound is similar to that of its trimethyl ether, $C_6H_3(OCH_3)_3$, which, of course, can have only the phenolic structure. Hence they concluded that, when in the free state, phloroglucinol possesses the structure of a true phenolic compound [formula (*i*)].

Another example is that of **ethyl acetoacetate** which exhibits *keto-enol tautomerism* :

$$CH_3.CO.CH_2.COOC_2H_5 \rightleftharpoons CH_3.C(OH){=}CH.COOC_2H_5$$

The spectrum of the ester is found to possess no bands, whereas its metallic derivatives show a strongly banded absorption. Further, the addition of an alkali to the ester causes a banded spectrum to appear which becomes more and more prominent as the quantity of the alkali added is increased. Now, the metallic derivatives of the ester must be regarded as being derived from the enolic form. Hence, the ester itself must consist mainly of the *ketonic* form.

8. Dipol Moments.—A molecule is an assemblage of protons and electrons, the former being electropositive and the latter electronegative. The electrical centre of the electrons and that of the protons in a molecule may or may not coincide with each other. Hence, under the influence of an external electric field, the molecules of the former type will not be affected. But in the latter case, they will behave as **electrical doublets** or **dipoles.** They will have a definite turning moment, and will therefore tend to arrange themselves in such a way as to give rise to a system of minimum potential energy. This tendency will, of course, be opposed by the thermal energy of the molecules.

The magnitude of the turning moment of a dipolar molecule depends on the magnitude of the charge at each pole and the distance between them. As the charge at each pole is equal in magnitude, we may define the **dipole moment,** μ, as the magnitude of the charge, z, multiplied by the distance, d. Thus, we have :

$$\mu = z \times d$$

where the charge, z, is expressed in electrostatic units and the distance, d, in angstroms ($A = 10^{-8}$ cm.). The charge on an electron, or the elementary electric charge, is $4{\cdot}8 \times 10^{-10}$ electrostatic units. Hence, an electron separated from a unit positive charge by a distance of 1 angstrom has a dipole moment

$$= 4{\cdot}80 \times 10^{-10} \times 10^{-8} \text{ esu/cm.}$$

$$= 4{\cdot}80 \times 10^{-18} \text{ esu/cm.}$$

$$= 4{\cdot}80 \text{ Debye units.}$$

For the sake of convenience, a dipole moment of 10^{-18} e.s.u./cm. is called **a debye unit** or a **debye.**

The dipole moments are determined experimentally by a variety of methods, which we need not consider here.

The following table gives the dipole moments of some substances in Debye units (10^{-18} e.s.u./cm.)

Dipole Moments of Polar Compounds.

Inorganic compounds	μ	*Aliphatic compounds*	μ	*Aromatic compounds*	μ
HCl	1·03D	CH_3Cl	1·45	C_6H_5Cl	1·73
HBr	0·78	CH_3Br	1·85	C_6H_5Br	1·71
HI	0·38	CH_3I	1·35	C_6H_5I	1·20
H_2O	1·84	CH_3OH	1·68	C_6H_5OH	1·7
H_2S	1·10	$(C_2H_5)_2O$	1·14	$(C_2H_5)_2O$	1·15
NH_3	1·46	C_2H_5OH	1·70	$C_6H_5COC_6H_5$	2·95
HCN	2·93	C_2H_5CHO	2·7	C_6H_5CN	4·37
SO_2	1·6	C_2H_5CN	3·3	$C_6H_5NO_2$	4·23
H_2O_2	2·1	$C_2H_5NO_2$	4·0	$C_6H_5NH_2$	1·56

Molecules with Zero Dipole Moment.—

Certain molecules possess a zero dipole moment ; *e.g.*

H_2, N_2, I_2, Br_2,
CO_2, CS_2, BCl_3, $SnCl_4$
CH_4, CCl_4, Benzene, Cyclohexane.

Such molecules possess a centre of symmetry so that they have no **resultant dipole moment.**

9. **Dipole Moments and Molecular Structure.**—Dipole moments, being vector quantities, may be added up vectorially, *i.e.*, in the same manner as we calculate the resultant of two or more forces by the application of parallelogram or triangle of forces. By the use of this method, dipole moments of various linkages have been determined.

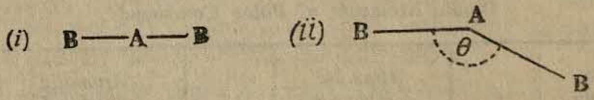
The following are some simple illustrative examples of the use of dipole moments in the study of molecular structure.

(1) Monatomic gases of the helium family are non-polar, as in their case no dipole is possible.

(2) Diatomic molecules of elements, too, are all non-polar.

(3) Diatomic molecules of compounds, so far examined, are all polar, *e.g.*, HCl, HBr, etc.

(4) Triatomic molecules may be either symmetrical or unsymmetrical. In the former case, the dipole moment is zero and in the latter it has a finite value. Thus, a molecule of the type AB_2, with the atom A lying in between the two B atoms, may have two configurations :—



In case (*i*) the three atoms lie in one line and the molecule is non-polar. Carbon dioxide, O=C=O. and carbon disulphide, S=C=S, are examples of this type. In case (*ii*) one link forms an angle θ with the other ; here the dipole moment,

$$\mu = 2m.\cos\tfrac{1}{2}\theta$$

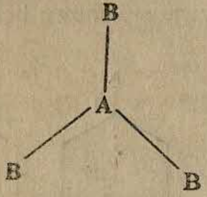
where m represents the moment of a single link. Water H_2O, and hydrogen sulphide, H_2S, represent molecules of this type. If the moment, m, of the link and the dipole moment, μ, of the compound are known, we can calculate the angle θ. Thus, in the case of water, m is 1·60 and μ 1·84. Substituting these values in the above equation, we get

$$1{\cdot}84 = 2 \times 1{\cdot}60 \times \cos\frac{\theta}{2}$$

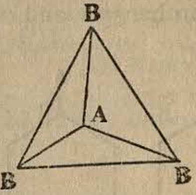
whence, $$\theta = 109° - 24'.$$

(5) Tetratomic molecules of the type AB_3 may either have all the four atoms lying in one plane with angles between the bonds all equal, as shown for configuration (*iii*). In such a case the molecule is *non-polar*. On the other hand, if the configuration is pyramidal (as shown in case *iv*), one of the atoms will be out of the plane of the other three, and the molecule, therefore, will be polar.

(*iii*)



(*iv*)



Boron trichloride, BCl_3 ($\mu=0$), is an example of the former type, and NH_3, PH_3, AsH_3, PCl_3, etc. of the latter type.

(6) Dipole moments have also proved useful in dealing with **cis-trans isomerism** among unsaturated compounds. The *trans*-compounds in which the centres of the positive and negative charges coincide, have a dipole moment equal to zero. The cis-isomers, on the other hand, possess a finite dipole moment. A few illustrative examples are tabulated below :—

	cis-isomer	*trans-isomer*
s-Dichloroethylene[1]	$\begin{array}{c}\text{H—C—Cl}\\ \| \\ \text{H—C—Cl}\\ \mu=1{\cdot}9\text{ esu.}\end{array}$	$\begin{array}{c}\text{H—C—Cl}\\ \| \\ \text{Cl—C—H}\\ \mu=0\end{array}$
s-Dibromoethylene	$\begin{array}{c}\text{H—C—Br}\\ \| \\ \text{H—C—Br}\\ \mu=1{\cdot}4\text{ D}\end{array}$	$\begin{array}{c}\text{H—C—Br}\\ \| \\ \text{Br—C—H}\\ \mu=0\end{array}$
s-Di-iodoethylene	$\begin{array}{c}\text{H—C—I}\\ \| \\ \text{H—C—I}\\ \mu=0{\cdot}8\end{array}$	$\begin{array}{c}\text{H—C—I}\\ \| \\ \text{I—C—H}\\ \mu=0\end{array}$
s-Chlorobromoethylene	$\begin{array}{c}\text{H—C—Cl}\\ \| \\ \text{H—C—Br}\\ \mu=1{\cdot}6\end{array}$	$\begin{array}{c}\text{H—C—Cl}\\ \| \\ \text{Br—C—H}\\ \mu=0\end{array}$

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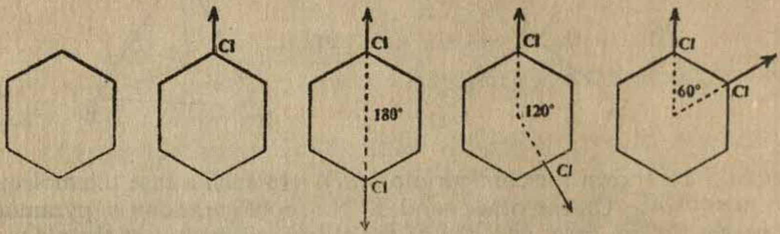
[1] The unsymmetrical isomers, *e.g.*, $H_2C=CCl_2$, do not exhibit cis-trans isomerism. They are readily differentiated from the symmetrical isomers by their *chemical* properties.

(7) Determination of dipole moments of **disubstitution products of benzene** has yielded important results. The **observed dipole moments** (in debye units) of benzene, chlorobenzene, *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene are shown below :—



Benzene	Chlorobenzene	*p*-Dichlorobenzene	*m*-Dichlorobenzene	*o*-Dichlorobenzene
$\mu=0$	$\mu=1{\cdot}55$	$\mu=0$	$\mu=1{\cdot}55$	$\mu=2{\cdot}27$

The **calculated values** deduced from the dipole moment of chlorobenzene ($\mu=1{\cdot}55$) with the help of the above figures are :—

For *para*-isomer $=\mu-\mu=0$
For *meta*-isomer $=2\times1{\cdot}55\times\cos 60°=1{\cdot}55$
For *ortho*-isomer $=2\times1{\cdot}55\times\cos 0°=2{\cdot}69$.

The figures for nitrobenzene and the three **dinitrobenzenes** are :—

	Observed	*Calculated*
Nitrobenzene	3·8	—
p-Dinitrobenzene	0·3	0
m- ,,	3·75	3·80
o- ,,	6·02	6·5

From the above data, we may draw the following conclusions :—

(1) The dipole moments increase progressively as the molecules become more and more unsymmetrical.

(2) The agreement between the observed and the calculated values, so far as the *meta*- and *para*- derivatives are concerned, is quite satisfactory, indicating the correctness of the **hexagonal formula for benzene** derived from chemical considerations.

(3) In the case of the *ortho*-derivatives, however, the deviations are distinctly greater than the error of observation, and indicate an interaction between the two neighbouring substituents.

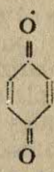
QUESTIONS

1. What are the different types of physical properties ? How is parachor useful in determining the structures of organic compounds ? (*Baroda, B.Sc., 1956*)

2. What is meant by colligative, additive and constitutive properties ? Give examples of each and explain briefly how they are related to the composition and structure of molecules of substances. (*Travancore, B.Sc., 1954*)

3. Write an essay on the relation between physical properties and chemical constitution. (*Madras, B.Sc. 1955* ; *Andhra B.Sc., 1955*)

4. What do you understand by parachor ? How is it related to surface tension ? For quinone, $C_6H_4O_2$, the two constitutions, I and II, shown in the margin, have been proposed. The experimental value for parachor of quinone is 237. (Parachor value for H = 17·1, C = 4·8, O = 20, for double bond 23·2, for a ring of six carbon atoms 6·1). Which constitution would you accept ? (*Agra, B.Sc. 1952*)



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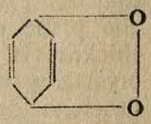


II

5. Explain "Molecular Refractivity". Give examples to illustrate its relation to chemical constitution. (*Osmania, B Sc., 1955*)

6. How is optical activity measured and what is the importance of this measurement in Chemistry ? (*Punjab, B.Sc., 1944*)

7. What is a polar molecule ? How is its dipole moment determined ? What information can dipole moments furnish about the structure of molecules ? Give examples. (*Kerala, B.Sc., 1957*)

8. Write notes on :—(*a*) Parachor, (*b*) Molecular refraction. (*Madras, B.Sc., 1953*)

9. Write a short note on Parachor and chemical constitution. (*Jammu and Kashmir, B.Sc., 1954*)

10. What do you understand bv parachor and dipole moment of molecules ? What is their importance in the study of chemical structure ? (*Aligarh, B.Sc. 1958*)

11. Write notes on the following with special reference to their significance in molecular structure : (*i*) Parachor ; (*ii*) Optical rotation. (*Lahore, B.Sc. 1958*)

12. What is meant by 'parachor' ? How is its determination helpful in the elucidation of molecular structure ? (*Punjab, B.Sc., 1959*)

13 Define the term "dipole moment", and outline one method of determining it. Show how the dipole moments have been employed to determine the structure of simple molecules. (*Bombay, B.Sc., 1951*)

14. Write a short account of the application of absorption spectra in the elucidation of molecular structure. Give illustrative examples.

15. Describe and discuss the influence of unsaturation and conjugation on the physical properties of organic compounds. (*Bombay, B.Sc., 1941*)

CHAPTER SEVEN

STEREOCHEMISTRY

1. Discoveries of Biot, Haüy and Herschel.—In 1813, Biot showed that thin plates of quartz, cut at right angles to the main axis, turned the plane of polarization of light through angles proportional to the thickness of the plates. He also noticed that while some quartz crystals gave plates having a dextro-effect on the polarized light, others yielded plates having a levo-effect. In 1815, he made the further important observation that certain organic substances, *e.g.*, turpentine oil, solutions of cane-sugar and tartaric acid, also possessed the power of turning the plane of polarization of light. Since then, many more optically active inorganic substances, *e.g.*, sodium chlorate, sodium bromate and ammonium lithium sulphate, and a far greater number of optically active organic substances have been discovered.

Biot found that a fundamental difference existed between optically active inorganic and organic substances. The former exhibit this activity only in the crystalline form, while the latter show it in the liquid and even in the gaseous state. Thus, if the crystalline forms, of quartz or sodium chlorate be destroyed by fusion or solution, the optical activity at once disappears. This is not so in the case of cane-sugar or tartaric acid ; solutions of these substances are optically active. Hence, Biot concluded that in quartz, etc., the optical activity is due to the *arrangement* of the crystalline particles, while in tartaric acid, etc., it is due to the *constitution* of the molecule.

The famous crystallographer Haüy had shown that the fully developed "hemihedral" quartz crystals existed in two closely related forms having certain characteristic facets, or faces, which in the case of one form lay to the right and in the other to the left, the two kinds of crystals being related as an object to its image, or as a right hand to a left hand. In the terminology of crystallography, they are said to be **enantiomorphous** (Gk. *enantios*, opposite ; *morphe*, form).

In 1820, Herschel correlated the observations of Haüy and Biot, and showed that plates cut from quartz crystals having right-handed hemihedral facets turned the plane of polarization to the right and those having left-handed hemihedral facets turned it towards the left. Thus a useful relation between hemihedrism and optical rotation of crystalline substances was discovered.

2. Pasteur's work on Tartaric Acids.—Tartaric acid obtained from grape-juice is optically active and turns the plane of polarization of light to the right. The mother liquor obtained in the purification of this acid contains another acid called **racemic acid**, which, since it possesses exactly the same *chemical* properties as tartaric acid, must have the same structure as the latter. However, racemic acid differs from tartaric acid in its *physical* properties, and is optically inactive.

In 1844, Mitscherlich published the results of his crystallographic examination of the sodium-ammonium salts of tartaric and racemic acids. He stated that these double salts "have the same chemical composition, the same crystalline form with the same angles...but the dissolved tartrate deviates the plane of polarization, while the racemate is indifferent."

"This note of Mitscherlich's," says Pasteur, "attracted my attention forcibly at the time of its publication. I was then a pupil in the *Ecole Normale*. Reflecting in my leisure moments on these elegant investigations of the molecular constitution of substances, and having reached—as I thought at least—a thorough comprehension of the principles generally accepted by physicists and chemists, the above note disturbed all my ideas. What precision in every detail ! Did two substances exist which had been more fully studied and more carefully compared as regards their properties ? But how, in the existing condition of the science, could one conceive of two substances so closely alike without being identical ?"

Pasteur had once wondered whether the organic substances possessing optical activity in solution would show hemihedrism in their crystals. He had found that tartaric acid, which is optically active, *did* form hemihedral crystals, while racemic acid, which is optically inactive, did *not* show this phenomenon. "Hence," says Pasteur, "I thought at once that Mitscherlich was mistaken on one point. He had not observed that his sodium-ammonium tartrate was hemihedral while his racemate was not. If this is so, the results in his note are no longer extraordinary ; and further, I should have, in this, the best test of my preconceived idea as to the inter-relation of hemihedry and the rotatory phenomena."

In 1846, Pasteur proceeded to re-investigate the problem. The result of his research may be stated in his own words :—

"I hastened, therefore, to reinvestigate the crytalline form of Mitscherlich's two salts. I found, as a matter of fact, that the tartrate was hemihedral, like all the other tartrates which I had previously studied, but. strange to say, the racemate was hemihedral also. Only, the hemihedral faces, which in the tartrate were all turned the same way, were, in the racemate, inclined sometimes to the right and sometimes to the left (Fig. 1 *A* and *B*). In spite of the unexpected character of this result, I continued to follow up my idea. I carefully separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined their solutions separately in the polarizing apparatus. I then saw with less surprise than pleasure that the crystals hemihedral to the right deviated the plane of polarization to the right, and those hemihedral to the left deviated it to the left, and when I took an equal weight of each of the two kinds of crystals, the mixed solution was indifferent towards the light in consequence of the neutralization of the two equal and opposite individual deviations."

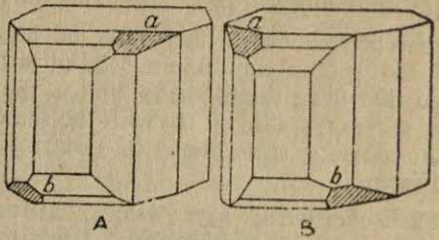


Fig. 1. Crystals of (*A*) Sodium ammonium *d*-tartrate, (*B*) Sodium ammonium *l*-tartrate

Pasteur's announcement of the above discovery was received at first with incredulity by the scientific world, and the French Academy of Sciences delegated Biot, the greatest living authority on polarized light, to examine Pasteur's statements. An account of the dramatic scene which followed has been left on record by Pasteur himself :—

"He [Mr. Biot] sent for me to repeat before his eyes the several experiments. He gave me racemic acid which he had himself previously examined and found to be quite inactive to polarized light. I prepared from it in his presence the sodium ammonium double salt, for which also he desired *himself* to provide the soda and ammonia. The liquid was set aside for slow evaporation in one of the rooms of his own laboratory, and when 30 to 40 grams of crystals had separated he again summoned me to the College de France, so that I might collect the dextro- and levo-rotatory crystals before his eyes, and separate them according to their crystallographic character, asking me to repeat the statement that the crystals which I should place on his right hand would cause deviation to the right, and the others to the left. This done, he said that he himself would do the rest. He prepared the carefully weighed solutions, and at the moment when he was about to examine them in the polarimeter, he again called me into his laboratory. He first put the more interesting solution, which was to cause rotation to the left, into the apparatus. Without making a reading but already at the first sight of the colour tints presented by the two halves of the field in the Soleil saccharimeter, he recognized that there was a strong levorotation. Then the illustrious old man, who was visibly moved, seized me by the hand, and exclaimed : "My dear child, I have so loved the sciences throughout my life that this makes my heart leap with joy !"

Pasteur further discovered that of the two kinds of crystals obtained from sodium ammonium racemate, the one showing dextrorotation gave an acid identical with natural tartaric acid in every respect, whereas the other gave an acid which in aqueous solution showed levo-rotation On mixing concentrated solutions of equal amounts of the *d*- and *l*-tartaric acids obtained as above, a precipitate of optically inactive racemic acid was at once formed. Thus, Pasteur was able to show both analytically, and synthetically, that recemic acid is a mixture of equal quantities of tartaric acid obtained from grapes and the hitherto unknown *l*-tartaric acid. For this reason, racemic acid is also called *dl*-**tartaric acid.**

Pasteur found that *d*- and *l*- tartaric acids were identical in crystalline forms, melting-point and solubility. The only two points in which they differ from each other are : (*a*) their rotatory powers which are equal but opposite and (*b*) the disposition of the hemihedral facets of their crystals, which are related to one another as an object and its image. Pairs of chemically identical substances related in this manner are called **optical isomers, optical antipodes, enantiomers or enantiomorphs.**

At the time of Pasteur's researches, the theory of molecular structure of Kekule had not yet been pronounced. It was, therefore, not possible to represent structurally the *d*- and *l*-tartaric acids. However, Pasteur's keen judgment led him to conclude that the molecules of the two tartaric acids possessed identical composition and structures, but that they differed in spatial arrangement so that one was the mirror image of the other.

3. Wislicenus' View on Isomerism of Lactic Acids.—In 1863, Wislicenus published a remarkable memoir on the synthesis of lactic acid. His method consisted in acting upon ethylene chlorohydrin with potassium cyanide and hydrolysing the nitrile so formed. In 1780, Scheele had discovered lactic acid in sour milk, and, in 1807, Berzelius obtained a similar acid, called **sarcolactic acid** from muscle juice. The acid was found to differ from the sour-milk acid in being dextro-rotatory, the former being optically inactive. Chemically, the two acids were found to be identical, though they differed in certain physical properties (see table under Lactic Acid). Wislicenus meditated upon this remarkable fact for several years, and in 1873, expressed the following view : "If it is once granted that molecules can be structurally identical and yet possess dissimilar properties, it can only be explained on the ground that the difference is due to a different arrangement of their atoms in space."

4. Le Bel and van't Hoff's Theory.—Stimulated by the work of Pasteur and of Wislicenus, a "space theory" of the isomerism of optically active compounds was developed independently and almost simultaneously in 1874 by Le Bel and van't Hoff. According to this theory, *the four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron, constructed around the carbon atom as centre.*

By reference to Fig. 2 it can be readily seen that if the four solid angles of the tetrahedron are occupied by four *different* atoms or groups (*a*, *b*, *c* and *d*), the resulting configuration is capable of existing in a right-handed form and a left-handed form. The mirror-image relationship of the molecule is repeated in the optical and crystallographic properties of the substances. The stereochemical figures, such as those given in Fig. 2, are called **space formulae.** By reference to these it will be seen that *the molecule of an optically active compound possesses no plane of symmetry.*

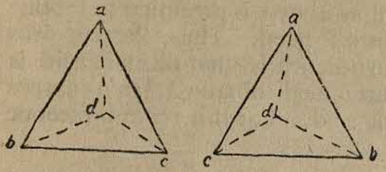


Fig. 2.

A carbon atom linked to four different atoms or groups is known as an **asymmetric carbon atom.** Of course, it is not the atom itself that is asymmetric, but the molecule that contains it. The stereoisomerism exhibited by compounds containing one or more asymmetric carbon atoms is called **optical isomerism**, since it is associated with optical activity and is to be distinguished from *geometrical isomerism* (sec. 13), which is not necessarily associated with optical activity.

Evidence in Favour of the Theory.—

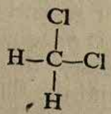
Let Bel and van't Hoff's theory of stereoisomerism is supported by the following facts:—

(1) All substances capable of existing in optically active forms possess one or more asymmetric carbon atoms (or asymmetric atoms of some other element, such as nitrogen etc.)

(2) If by any means the asymmetric character of the molecule is destroyed, [*e.g.*, in the case of lactic acid, $CH_3.CH(OH).COOH$, by reduction to propionic acid, $CH_3.CH_2.COOH$], the optical activity also disappears.

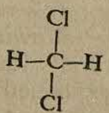
(3) The absence of isomeric forms of such substances as methylene chloride, CH_2Cl_2, which, if all the four carbon valencies lay in the same plane, should exist in two forms:

(*i*)



$H{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}{-}Cl$

and (*ii*)



$H{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}{-}H$

In spite of much research, no such isomerism has been found to exist.

(4) Bragg's X-ray analysis of the structure of diamond shows that in this substance the carbon atoms are united by tetrahedrally directed valency bonds (Fig. 3).

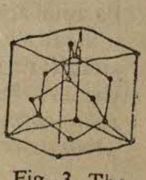
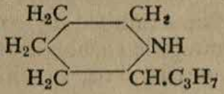


Fig. 3. The Diamond Lattice.

5. Stereoisomerism of compounds containing One Asymmetric Carbon Atom.—The more familiar examples of compounds containing one asymmetric carbon atom are:—

Lactic acid,	$CH_3.CH(OH).COOH$
Mandelic acid,	$C_6H_5.CH(OH).COOH$
Malic acid.	$COOH.CH(OH).CH_2.COOH$
Coniine,	

Each of these compounds can exist in three forms, two of which are optically active and the third optically inactive. Of the two optically active forms, one is dextrorotatory and the other levorotatory. These two forms turn the plane of polarization through the *same* angle, though in *opposite* directions. With the exception of this point, the two isomerides possess exactly identical properties. The third form is produced by mixing equimolecular quantities of *d*- and *l*- forms and is optically inactive, owing to the mutual, or, as we say, **external compensation** of the two constituents. An inactive product of this type is called a **racemic compound, a racemic mixture** or *racemic solid solution* (see sec. 10). When in the crystalline state, the racemic-form is frequently a definite compound having double the molecular weight of the *d*- or the *l*- modification. A racemic compound may be resolved into its optically active components by methods described in sec. 11.

6. Compounds containing Two Asymmetric Carbon Atoms.—A compound containing two *dissimilar* asymmetric carbon atoms is capable of existing in 2^2, or 4, optically active forms, made up of two pairs having equal and opposite rotatory power ; in addition to these, there exist two inactive racemic forms. Representing the two carbon atoms by *A* and *B* and their different spatial configurations by signs + and −, the four optically active forms are—

(1)	(2)	(3)	(4)
+A	−A	+A	−A
+B	−B	−B	+B

An example of this class is $C_6H_5.CHBr.CHBr.COOH$, **α, β-dibromophenylpropionic acid**, which exists in six forms, four active and two racemic.

Compounds containing two structurally *similar* asymmetric carbon atoms can have three configurations. In this case A = B, and hence the configurations (3) and (4) of the preceding case become identical :

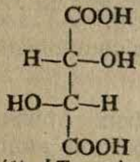
(1)	(2)	(3)
+A	−A	+A
+A	−A	−A

Modifications (1) and (2) are optically active while (3) is inactive by, what is termed, **internal compensation**, the dextro-rotatory effect of one of the asymmetric carbon atoms being exactly counterbalanced by the levorotatory effect of the other. A compound of this type is described as *i*-, or *meso*-compound, and, unlike a racemic compound, is non-resolvable.

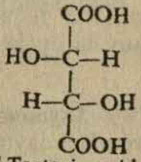
In addition to the above three forms, there exists another inactive (racemic) form containing equivalent quantities of the active enantiomorphs, the inactivity here being due to *external* compensation.

The best known example of isomerism exhibited by compounds containing two structurally similar asymmetric carbon atoms is furnished by dihydroxysuccinic acid, or **tartaric acid**, which exists in four forms. As already mentioned, the acid derived from grape juice is *d*-tartaric acid. The optically inactive **racemic acid**, obtained from the mother liquor of *d*-tartaric acid, is the *dl*-acid formed by the admixture of equivalent quantities of *d*- and *l*-tartaric acids. It can be resolved into its *d*- and *l*- constituents by mechanical separation of the hemihedral crystals of its sodium ammonium salt, followed by treatment of the two kinds of crystals with a mineral acid. The internally compensated form, known as **mesotartaric acid**, is readily obtained (along with *dl*-tartaric acid) by heating *d*-tartaric acid with a little water at 165°.

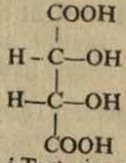
The four isomers are represented by the following projection formulæ[1] :—



$$\begin{array}{c}COOH\\ |\\ H-C-OH\\ |\\ HO-C-H\\ |\\ COOH\end{array}$$



$$\begin{array}{c}COOH\\ |\\ HO-C-H\\ |\\ H-C-OH\\ |\\ COOH\end{array}$$



$$\begin{array}{c}COOH\\ |\\ H-C-OH\\ |\\ H-C-OH\\ |\\ COOH\end{array}$$

(1) *d*-Tartaric acid (2) *l*-Tartaric acid

(4) *dl*-Tartaric acid or Racemic acid

(3) *i*-Tartaric or Meso-tartaric acid

The properties of the four acids are given in on page 111.

7. Compounds containing more than two Asymmetric Carbon Atoms.—The number of possible stereoisomerides increases rapidly with an increase in the number of asymmetric carbon atoms. A compound containing *n* asymmetric carbon atoms, each of which is structurally *different* from all the rest, can exist in 2^n stereoisomeric forms, consisting of a number of pairs of mirror-image isomerides having equal and opposite rotations. If two, or more of the carbon atoms be structurally identical, some of the possibilities of isomerism will vanish as in the case of tartaric acids.

8. Physiological Distinction between Optical Antipodes.—In their physiological action the optical isomers show a profound difference. Thus *l*-nicotine, which is obtained from tobacco leaves, when injected into the blood of an animal produces pain, excitation, and finally death. The *d*-nicotine, on the other hand, which can be obtained synthetically, causes only a strong temporary shivering when similarly injected. Several other cases of antipodes showing profound difference in their physiological action are known.

---

[1] The projection formula of an internally compensated stereoisomeride is identical with its mirror image ; hence it can be made to coincide with the latter by rotation in the plane of the paper. If the projection formula of a stereoisomeride is not identical with its mirror image, *i.e.*, if it cannot be made to coincide with the latter by rotation in the plane of the paper, it evidently represents an optically active stereoisomeride, the mirror-image representing the projection formula of the optical antipode.

Pasteur explained this difference in physiological action by assuming that the nerve and tissue components of our bodies are themselves asymmetric, and consequently react differently towards dextro- and the levo-isomerides. Similar differences of a biochemical nature have been observed in the behaviour of optical antipodes towards ferments, and are utilized in the separation of racemic compounds into their optically active components.

Properties of four Tartaric Acids

Property	*d*-Tartaric acid	*l*-Tartaric acid	*i*-Tartaric (or Mesotartaric) acid	Racemic (*dl*-) acid
1. Crystals.	Monoclinic, anhydrous prisms; *m.p.* 170°; show hemihedral facets.	Same as the *d*-acid, except that the hemihedral facets are turned in the opposite direction to those in *d*-acid.	Rectangular, efflorescent plates contain $1H_2O$; *m.p.* 143°; show no hemihedral facets.	Rhombic, efflorescent crystals; contain $1H_2O$; *m.p.* 206°; show no hemihedral facets.
2. Action on polarized light.	Dextrorotatory.	Levorotatory.	Inactive (by internal compensation).	Inactive (by external compensation).
3. Sodium ammonium salt.	Crystals show hemihedral facets.	Crystals show hemihedral facets turned in the opposite direction to those in the *d*-tartrate.	Crystals show no hemihedral facets.	Two kinds of crystals, some hemihedral to the right, others to the left; mechanically separable.
4. Potassium hydrogen salt.	Sparingly soluble in water.	Sparingly soluble in water.	Readily soluble in water.	Readily soluble in water.

9. Racemization.—As already mentioned, *d*-tartaric acid, when heated with water under pressure, yields racemic acid. If *l*-tartaric acid be similarly treated, we get the same result. Many other optically active substances pass into the externally compensated forms when submitted to the action of heat or chemical reagents. Such a process of inactivation is called "racemization".

Racemization may be effected by the following means :

(1) Some substances (*e.g.*, amyl alcohol, limonene, pinene) get racemized on being merely *heated* to a sufficiently high temperature.

(2) In certain cases, heating with *water* brings about racemization. Thus, *d*-tartaric acid is transformed, under this treatment, into a mixture of racemic acid and meso-tartaric acid.

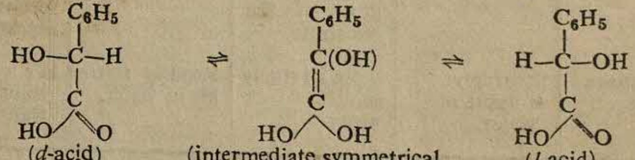
(3) Optically active acids in which the asymmetric carbon atom has hydrogen attached to it and occupies the *alpha* position with respect to the carboxyl group [*e.g.*, mandelic acid, $C_6H_5.CH(OH)-COOH$] are readily racemized in the presence of an *alkali.*

(4) In certain cases (*e.g.*, *d*-valeric acid and limonene), racemization is induced by *sulphuric acid.*

(5) Certain substances [*e.g.*, esters of bromosuccinic acid and of phenyl bromoacetic acid] get completely racemized in the course of time at the ordinary temperature. This phenomenon, first observed by Walden and termed "**auto-racemization**", has now been shown to be due to the presence of impurities (*e.g.*, HBr), which act catalytically. If these impurities are *completely* eliminated no racemization occurs.

Werner explains the phenomenon of racemization by imagining that each of the four groups attached to the asymmetric carbon atom is in oscillation within the independent orbit. Under the influence of a recemizing agent the amplitude of the oscillation is increased, with the result that a mutual invasion of the orbits occurs. This makes it possible for the *d*-form to pass into the *l*-form, and *vice versa.* A dynamic equilibrium between the two forms is thus established when an equal number of the two kinds of molecules have been produced.

According to Lowry and others, racemization is due to slight isomerization of the asymmetric molecule into another that is not asymmetric. The latter form constitutes the unstable intermediate product, which, being in dynamic equilibrium with the two optically active forms, yields an equimolecular mixure of the two. Thus, the racemization of mandelic acid is represented by Lowry as under :—



(*d*-acid) (intermediate symmetrical form) (*l*-acid)

10. Nature of Racemic Modifications in the Solid State. The enantiomorphic modifications (*d*- and *l*-) may occur in equimolecular proportions to constitute what is known as a **racemic form.** Three cases are possible :

(*i*) a racemic **'conglomerate'** or '*mixture*' of *d*- and *l*-isomers in equimolecular proportions (Type I).

(*ii*) a **racemic compound** (*dl*), composed of one molecule of each of the optical and opposite isomers (Type II).

(*iii*) a racemic **'solid solution'** or **'mixed crystals'** of equimolecular proportions of *d*- and *l*- forms (Type III).

There are three methods of distinguishing racemic forms: two of them, due to Roozeboom[1] and Bruni[2], based on phase rule, are physical, *viz.*, freezing-point (or melting-point) and solubility methods. The third method—'Biochemical'—is due to Singh *et al*[3].

11. (1) **Solubility-Composition Diagrams.** Roozeboom and Bruni have theoretically discussed, from the standpoint of *phase-rule*, the solubility relationships of optically active isomers, their racemic mixtures, compounds and solid solutions. The solubility composition isotherms, which they had deduced theoretically, had not been obtained experimentally, until Singh and Perti[4] in the case of camphor β-sulphonic acid and Singh and Nayar[5] in the case of camphoric acid and camphor carboxylic acid supplied these experimental curves. In each case *three* curves are obtained which conclusively proves that the racemic acids are true *dl*-compounds (compare melting point-composition diagrams for racemetes given on the side).

(2) **The Melting Point-Composition Method of Roozeboom.** This method consists in preparing the Melting point-composition Diagram. On the composition axis are given the percentage compositions of mixtures of the *dextro*-(or *laevo*-) and the racemic-forms and on the melting-point axis their melting-points. As the diagrams are symmetrical, only one of the active forms is needed for the study.

In the case of a racemic mixture (Type I), the melting point of each optical isomer will be lowered by the addition of the increasing amounts of the racemic *conglomerate* till the eutectic point (the melting-point of the racemic form) is reached. Thus there will be *two* symmetrical curves formed by joining the melting-points of each optical isomer and the racemic *conglomerate* (racemic mixture), as illustrated in Fig. 1.

In the case of the racemic compound (racemate), *three* curves will be obtained with two symmetrical eutectic points—invariant points—and a central maximum point

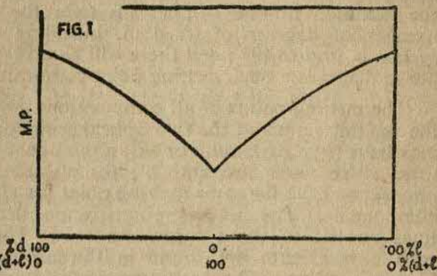


FIG. I

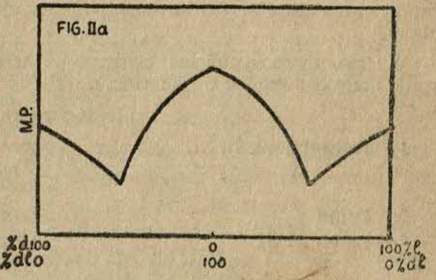


FIG. IIa

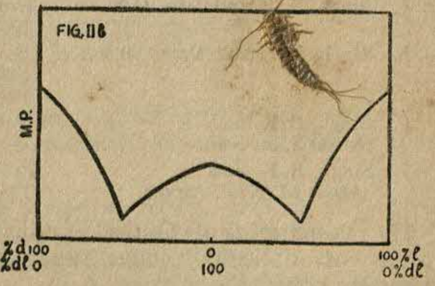


FIG. IIb

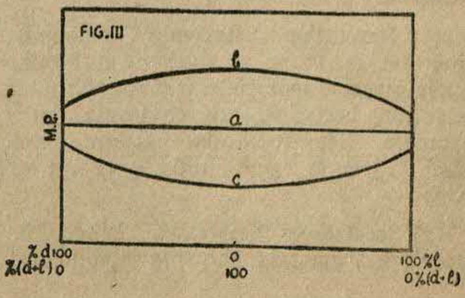


FIG. III

The pair of salts (unlike that obtained with an optically inactive base, such as sodium or ammonium hydroxide) is *not* enantiomorphous. The two salts, therefore, possess different solubilities and may be readily separated by fractional cystallization. The individual salts may then be decomposed by hydrochloric acid to obtain the two optically active acids. For example, Pasteur, in 1853, found that racemic acid when combined with quinine, a levo rotatory alkaloid, gives the far less soluble quinine *d*-tartrate and the fairly soluble quinine *l*-tartrate. With cinchonine, on the other hand, *l*-tartrate is found to be the less soluble salt; hence, on fractional crystallization, this salt separates out first.

Similarly, a racemic base may be separated into its optically active constituents by making it combine with an optically active acid, and submitting the resulting salts to fractional crystallization.

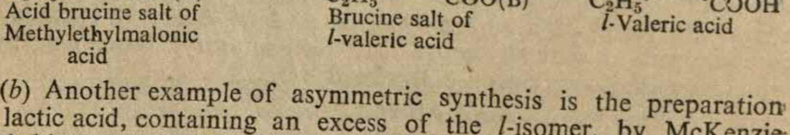
(2) **Asymmetric Synthesis.** As is well known, when a compound containing an asymmetric carbon atom is synthesised from substances having no asymmetric carbon atoms, the new product is always of the racemic type, *e.g.*,

$$\underset{\text{Benzaldehyde}}{C_6H_5.CHO} + HCN \longrightarrow \underset{dl\text{-Mandelonitrile}}{C_6H_5.CH(OH)CN}$$

On the other hand, if a compound containing an asymmetric carbon atom be synthesised under the influence of an *optically active grouping* which is subsequently removed, the product may exhibit optical activity. A synthesis of this type is called *asymmetric synthesis*.

Of the many asymmetric syntheses carried out by various investigators the following may be mentioned :—

(*a*) Marckwald in 1904, prepared an active *i*-valeric acid by heating at 170° the acid brucine salt of methylethylmalonic acid, until no more carbon dioxide was evolved. Representing the brucine molecule, $C_{23}H_{26}N_2O_4$, by B, the change may be represented as follows :—



$$\underset{\substack{\text{Acid brucine salt of}\\ \text{Methylethylmalonic}\\ \text{acid}}}{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}COOH\\COO(B)\end{matrix}} \xrightarrow{-CO_2} \underset{\substack{\text{Brucine salt of}\\ l\text{-valeric acid}}}{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\COO(B)\end{matrix}} \xrightarrow{HCl} \underset{l\text{-Valeric acid}}{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\COOH\end{matrix}}$$

(*b*) Another example of asymmetric synthesis is the preparation of lactic acid, containing an excess of the *l*-isomer, by McKenzie and his co-workers. This was effected by reducing *l*-menthyl (or *l*-bornyl) pyruvate with aluminium amalgam and water :

$$\underset{\text{Pyruvic ester}}{CH_3CO.COOR} \xrightarrow{2H} \underset{\text{Lactic ester}}{CH_3CH(OH).COOR} \xrightarrow{HCl} \underset{\text{Lactic acid}}{CH_3.CH(OH).COOH}$$

When the *d*-amyl ester of pyruvic acid was used, an excess of the *d*-lactic acid was formed.

(*c*) McKenzie and Wren found that when *l*-bornyl ester of fumaric acid is oxidized by means of potassium permanganate, a mixture of *d*- and *l*- tartaric esters, containing an excess of the latter, is formed. When the bornyl group is removed by treatment with hydrochloric acid, the levo-rotatory tartaric acid is obtained:

$$\begin{array}{l}\mathrm{CH.COOR}\\ \|\\ \mathrm{CH.COOR}\end{array} \xrightarrow{H_2O + O} \begin{array}{l}\mathrm{CH(OH).COOR}\\ |\\ \mathrm{CH(OH).COOR}\end{array} \xrightarrow{HCl} \begin{array}{l}\mathrm{CH(OH)COOH}\\ |\\ \mathrm{CH(OH)COOH}\end{array}$$

When *d*-bornyl fumarate is used, the product is found to contain excess of *d*-tartaric ester.

(*d*) Rosenthaler, in 1909, obtained *l*-mandelic acid by making benzaldehyde combine with hydrogen cyanide in the presence of the enzyme emulsin, and hydrolysing the resulting cyanohydrin :

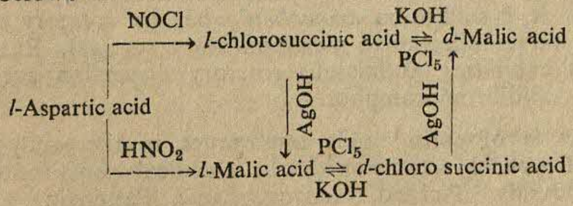
$$\underset{\text{Benzaldehyde}}{C_6H_5.CHO} \xrightarrow{HCN} \underset{l\text{-Mandelonitrile}}{C_6H_5.CH(OH).CN} \xrightarrow{H.OH} \underset{l\text{-Mandelic acid}}{C_6H_5.CH(OH).COOH}$$

(3) **Production of one Optical Antipode from another.** An optical isomer may be obtained from its antipode in two ways:

(*a*) The optical isomer available is first racemized (sec. 9) and the second isomer is then separated from the racemic mixture (sec. 12).

(*b*) **Optical Inversion** *or* **Walden Inversion.** Walden, in 1893, found that when one radical in an optically active compound is replaced by another, the configuration of the new compound may be influenced by the nature of the reagent employed. Thus, when *l*-chlorosuccinic acid is treated with silver hydroxide *l*-malic acid is formed, but if dilute potassium hydroxide be used to bring about the hydrolysis, *d*-malic acid is obtained. A change of configuration effected in this manner by means of suitable reagents is called "optical inversion" or "Walden inversion."

A complete scheme summarizing the observations of Walden is given below:


NOCl
KOH
l-chlorosuccinic acid ⇌ d-Malic acid
PCl5
l-Aspartic acid
AgOH
AgOH
HNO2
PCl5
l-Malic acid ⇌ d-chloro succinic acid
KOH

Emil Fischer, in 1911, showed that α-amino and α-halogen acids undergo optical inversion under suitable treatment. Many other cases of Walden inversion have been studied,[1] but no comprehensive explanation of the phenomenon has so far been offered.

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[1] See Bawa Kartar Singh's Presidential address to the 7th Session of Indian Science Congress, Section of Chemistry (1920) ; *Jour.*, and *Proc.*, Asiatic Society of Bengal, 1921, XVII, 213.

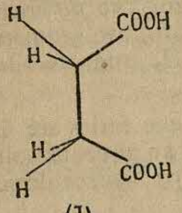
13. Rotatory Dispersion.—Biot found that the magnitude of the rotation of plane-polarized light depended on the wavelength of the light, and was approximately inversely proportional to the square of the wavelength, that is, $\left[\alpha\right]_{\lambda}^{T}=\frac{k}{\lambda^2}$, known as **Biot's Law**. This change of rotation with change of wavelength of the light is called **Rotatory Dispersion.** This law is obeyed in a very few cases, such as sodium tartrate, octyl oxalate and *p*-iodophenylacetylamino camphor.

Drude in 1897 expressed rotatory dispersion by the formula, $\left[\alpha\right]_{\lambda}^{T}=\Sigma\frac{k}{\lambda^2-\lambda_0^2}$, the summation containing several partial rotations of the type, $\frac{k'}{\lambda^2-\lambda_0'^2}$, $\frac{k''}{\lambda^2-\lambda''_0{}^2}$ etc. This formula applies only in the case of completely transparent media.

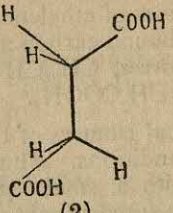
Lowry adopted this formula for classifying rotatory dispersion into **simple dispersion,** when it can be expressed by a single term, $\left[\alpha\right]_{\lambda}^{T}=\frac{k}{\lambda^2-\lambda_0^2}$, where k represents the '*rotation constant*' and λ_0^2 the '*dispersion constant*'. λ_0 corresponds to the '*characteristic wavelength*' of the dominant absorption band which governs the rotation of the compound. This formula holds good for many organic compounds, such as sucrose, camphorquinone, and asymmetric secondary alcohols. When the rotatory dispersion cannot be expressed by the *one-term* Drude's formula, but requires two or more terms, namely, $\left[\alpha\right]_{\lambda}^{T}=\frac{k'}{\lambda^2-\lambda'_0{}^2}+\frac{k''}{\lambda^2-\lambda''_0{}^2}$, it is called **'complex dispersion'**. It is *normal* when the specific rotation increases regularly with decreasing values of wavelength, as in the cases of camphor and camphor-β-sulphonic acid, whereas it is said to be '*anomalous*' when the rotatory dispersion curve shows an inflection, a maximum and a reversal. Examples of substances exhibiting anomalous rotatory dispersion are ethyl tartrate and α-, β-dibromocamphor.

This subject is of considerable importance in the study of the correlation of optical activity with the chemical constitution of organic compounds. Pickard, Kenyon, Rupe, Patterson, Lowry, Singh and others have worked extensively on this subject.

14. Geometrical Isomerism.—Whereas tartaric acid exhibits stereoisomerism, succinic acid does not, and is known only in one form. If the single bond that unites the tetrahedra representing the two carbon atoms were of a rigid type, the following two configurations for succinic acid would be possible. But, since the isomerism among symmetrical saturated substances of the above type is not known, it must be concluded that *there occurs a free rotation of* *carbon atoms about the single bond.* It is assumed that the atoms or groups united to the singly bound carbon atoms exert a mutual directive influence on each other, until, by virtue of free rotation about the common axis, the whole system acquires the most stable configuration.



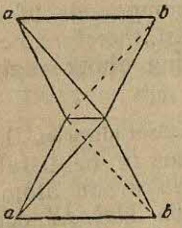
(1)



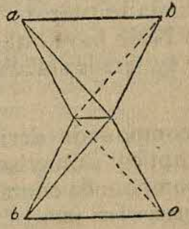
(2)

With compounds containing doubly bound carbon atoms, however, the case is otherwise. All independent rotation of the tetrahedra here ceases, as they are held together at *two* different points. Hence, compounds of the type $abC=Cab$ and also of the type $abC=Ccd$ are found to exist in the stereoisomeric forms having the configurations :

(1)

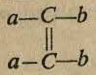


and (2)



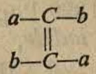
For the sake of convenience, these configurations are represented by projection formulæ as follows :—

(1)



$$\begin{array}{c} a-C-b \\ \| \\ a-C-b \end{array}$$

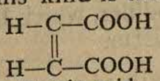
and (2)



$$\begin{array}{c} a-C-b \\ \| \\ b-C-a \end{array}$$

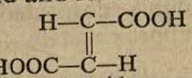
Compounds represented by configuration (1) *i.e.*, those in which similar groups lie on the same side of the molecule, are known as the *cis* isomers, while those represented by configuration (2), having similar groups on opposite sides, are called *trans*-isomers.

The most familiar example of the **cis-trans isomerism** or **geometrical isomerism** of this kind is that of maleic acid and fumaric acid :—



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

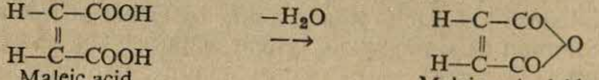
Maleic acid



$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

Fumaric acid

The two acids possess different physical constants. Moreover, they behave differently when heated. Maleic acid, on being heated, readily loses a molecule of water, yielding an anhydride, while fumaric acid does not. When the latter is strongly heated it is partially converted into the anhydride of maleic acid. Because of the ready formation of the anhydride, maleic acid is assigned the *cis*-formula and fumaric acid the *trans*-formula :



Maleic acid Maleic anhydride

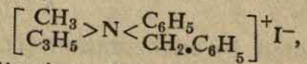
Other derivatives of ethylene containing two *different* groups linked to each doubly bound carbon atom, also show geometrical isomerism (*e.g.*, **dimethylethylenes**, $CH_3.CH=CH.CH_3$ and **crotonic and isocrotonic acids**, $CH_3.CH=CH.COOH$).

The geometrical isomers of the ethylene series are interconvertible under certain conditions. Thus, when an aqueous solution of maleic acid is heated with a small quantity of hydrochloric acid, it gets transformed into fumaric acid.

15. Stereochemistry of Nitrogen.—There are two groups of stereoisomeric nitrogen compounds, which are exactly analogous to the two classes of stereo-isomeric carbon compounds already described :—

(1) **Optically Active Nitrogen Compounds.** Although the three valencies of the trivalent nitrogen atom appear not to lie all in the same plane[1], all attempts to prepare optically active compounds of the general formula N*abc* have hitherto failed. It must, therefore, be concluded that the system is sufficiently mobile to bring about rapid racemization.

The compounds derived from **tetra-covalent nitrogen**, however, do exhibit optical isomerism. The case appears to be parallel to that of the compounds containing an asymmetric carbon atom. The **substituted ammonium salts** of the general formula N*abcdX* occur in two optically active forms of equal and opposite rotation, and an inactive racemic form containing equimolecular quantities of the *d*- and *l*-forms. Thus in 1899 Pope and Peachey resolved *methyl-allyl-phenyl-benzyl-ammonium iodide*,



$$\left[\begin{matrix}CH_3\\C_3H_5\end{matrix}>N<\begin{matrix}C_6H_5\\CH_2.C_6H_5\end{matrix}\right]^+I^-,$$

by fractional crystallization of its *d*-camphorsulphonates from a non-hydrolysing solvent (ethyl acetate or acetone). The *d*-camphorsulphonate of the *d*-base proved to be the less soluble salt. This salt and the *d*-camphorsulphate of the *l*-base were obtained pure. The two salts, on being separately treated with potassium iodide, gave the sparingly soluble substituted ammonium iodides, which had a specific rotation of approximately ± 52° in chloroform.

When a chloroform solution of the substituted ammonium iodide is warmed or allowed to stand for a few days, racemization takes place. This appears to be due to the dissociation of a molecule of the iodide followed by recombination in a different manner.

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[1] Singh, B.K., *Current Science*, 1938, *8*, *13* ; *Proc. Indian Acad. Sci.*, 1939 *91*, 323.

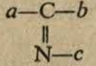
Several other compounds of the general formula N*abcdX* have been resolved by different investigators.

Another class of optically active nitrogen compounds, namely, the **amine oxides** of the general formula $O \leftarrow NR_1R_2R_3$, have been prepared and resolved by Meisenheimer.

A third class of optically active nitrogen compounds, namely, the **substituted quarternary azonium bases** of the general formula $[NR_1R_2R_3(NH_2)]OH$, have been prepared and resolved by Bawa Kartar Singh[1].

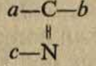
According to modern views, the nitrogen atom in the ammonium and substituted ammonium compounds is tetra-covalent and not pentavalent as was formerly supposed. The four valencies of the nitrogen atom, like those of the tetra-covalent carbon, are supposed to be directed towards the four angular points of a regular tetrahedron, at the centre of which the nitrogen atom itself lies. The stereochemistry of nitrogen is therefore strictly analogous to that of carbon.

(2) **Nitrogen Compounds showing Geometrical Isomerism.**—Starting from the consideration that a very large number of organic compounds exist in which a trivalent nitrogen atom takes the place of a CH-group (*e.g*, benzene, C_6H_6, and pyridine, C_5H_5N) Hantzsch and Werner came to the conclusion that the three nitrogen valencies occupy relative positions which are similar in direction to the three free valencies in the CH-group. Hence, when two nitrogen valencies are bound to one carbon atom, there results a case of geometrical isomerism which is exactly analogous to that of ethylene derivatives (Sec. 14) and which may be expressed by the following formulae :—



$$\begin{array}{lll} a- & C & -b \\ & \| & \\ & N & -c \end{array}$$

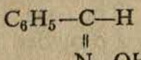
and



$$\begin{array}{lll} a- & C & -b \\ & \| & \\ c- & N & \end{array}$$

Numerous examples of this type of isomerism have been found among unsymmetrical oximes. Thus, benzaldoxime exists in the following two forms :

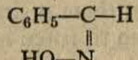
(*i*)



$$\begin{array}{lll} C_6H_5- & C & -H \\ & \| & \\ & N & -OH \end{array}$$

Benz-*syn*-aldoxime

(*ii*)



$$\begin{array}{lll} C_6H_5- & C & -H \\ & \| & \\ HO- & N & \end{array}$$

Benz-*anti*-aldoxime

The determination of the configuration of the stereoisomeric aldoximes was formerly based on the principle of intermolecular reaction between groups which are spatially contiguous. Accordingly, one of the forms which on being treated with acetic anhydride lost water, yielding a nitrile, was supposed to be the *syn*-isomer The other form, which did not lose water, was taken as the *anti*-isomer. This view, however, is contrary to the results obtained by Brady and Bishop (*Jour. Chem. Soc.*, 1925, 1357) in the case of the isomeric

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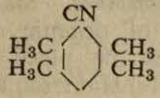
[1] J.C.S. 1913, **103**, 604 ; 1914, **105**, 1972 ; 1920, **117**, 1202.

2-chloro-5-nitro benzaldoximes. They conclude that the elimination of water from the unstable oxime occurs *trans*- or cross-ways. Similarly, Meisenheimer (*Ber.*, 1921, 3206, etc.) finds that it is the *anti*-form which loses the elements of water; consequently such reactions are *trans*- and not *cis*-eliminations, as previously believed.

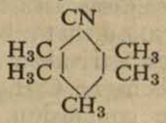
The configuration of the stereoisomeric ketoximes can be determined by means of the Beckmann transformation which always takes place by an *anti*- or *trans*-interchange (Mills, *British Association Report*, 1930). The subject, however, is beyond the scope of this book.

16. Steric Hindrance.—This is a stereochemical phenomenon unconnected with isomerism. It refers to the *influence exerted on a reacting group by the spatial disposition of neighbouring atoms.*

The first case of steric hindrance was discovered by Hofmann in 1872. It was found that certain aromatic tertiary amines, $R_1R_2R_3N$, where R_1,R_2, and R_3 are large groups, will not react with methyl iodide to form quaternary ammonium salts. In 1884, Hofmann found that tetramethyl- and pentamethyl-benzonitriles,



and

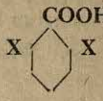


cannot be hydrolysed by the usual reagents. Since then, a large number of cases of steric hindrance have been observed by various investigators, and an explanation of this phenomenon has been offered.

It is assumed that each atom in a molecule vibrates about a certain mean position, and that the amplitude of the vibration is quite appreciable when compared with the size of the molecule itself. If this be so, the atom will require for its vibration a space somewhat larger than its own volume. It is quite easy to see that if another atom were to force its way into the vibration sphere of the first atom, collisions between the two will occur with the possible result that one of them is driven back. The case is similar to that of a person trying to force his way into a crowded room.

Now, in the case of a chemical reaction two or more groups are involved. These will react with one another only if they come within range of each other's attractions. If we surround one of the groups with such a mass of atoms that the other group or groups concerned in the reaction are unable to force their way in, we shall be able to hinder the progress of the reaction. Thus, in the case of tertiary amines, studied by Hofmann, the nitrogen atom is surrounded by groups (R_1, R_2, and R_3) that are of such a size as not to permit the methyl group of methyl iodide to come near the nitrogen atoms. Hence, no combination occurs. Similarly, the CN-group in tetramethyl- and pentamethyl-benzonitriles is protected from reaction by the crowding round it of the methyl groups.

Victor Meyer in 1894 found that di-*ortho*-substituted benzoic acids of the formula shown in the margin, in which X stands for CH_3, Cl, Br, NO_2, etc., form no ester (or very little of it) when treated with alcohol and hydrogen chloride. Further, if such an acid is once converted into its ester by other means (*e.g.*, by the interaction of its silver salt with an alkyl iodide), the ester can be hydrolysed only with extreme difficulty.



QUESTIONS

1. Write an account of Pasteur's work on tartaric acids.

2. Explain with appropriate examples van't Hoff and Le Bel's theory of asymmetric carbon atom. (*Punjab, B.Sc., 1960*)

3. Explain van't Hoff and Le Bel's theory of molecular configuration and show how it accounts for the different varieties of tartaric acid. (*Banaras, B.Sc., 1956*)

4. What is optical isomerism and what is it due to? How can racemic mixtures be resolved or optically active compounds synthesised? (*Lahore, B.Sc., 1958*)

5. Give an account of Pasteur's work on the tartaric acids. Describe the methods that can be employed for the resolution of racemic organic compounds? (*Travancore, B.Sc., 1956*)

6. Explain fully the term 'Stereoisomerism.' Discuss the stereoisomerism of tartaric acid. (*Allahabad, B.Sc., 1957*)

7. Define isomerism and explain with examples. Discuss briefly the isomerism shown by fumaric and maleic acids. (*Nagpur, B.Sc., 1956 ; Aligarh B.Sc., 1957*)

8. Write what you know about the optical isomerism of organic compounds. Illustrate with examples the theory underlying optical activity. (*Gauhati, B.Sc., 1957*)

9. Give a full account of the isomerism of tartaric acids. (*Andhra, B.Sc., 1958*)

10. Discuss with examples the various types of isomerism met with in organic chemistry, and discuss geometrical isomerism in detail. (*Lucknow, B.Sc., 1953*)

11. Under what conditions would an organic compound be expected to show optical activity? Indicate the different types of organic molecules which are capable of exhibiting this property. (*Madras, B.Sc., 1952*)

12. How would you account for the isomerism of tartaric acids? How can racemic acid be resolved into enantiomorphs? What theoretical explanation would you offer for the process? (*Punjab, B.Sc., 1950*)

13. Discuss the phenomenon of optical activity as shown by the isomerism of lactic acid. (*Madras, B.Sc., 1960*)

14. Discuss briefly the isomerism of tartaric acid. Outline a convenient method for the resolution of *racemic* tartaric acid into its optical isomers (*Calcutta, B.Sc., 1960*)

15. Explain and illustrate :—

(*a*) Enantiomorphs ; (*b*) Meso compound ; (*c*) Racemisation.

What methods are available for the resolution of racemic compounds? (*Utkal, B.Sc., 1960*)

16. Write notes on the following :—

(*a*) Walden Inversion ; (*b*) Asymmetric synthesis ; (*c*) Optical Resolution (*d*) Steric Hindrance. (*Jammu and Kashmir, B.Sc., 1960*)

17. What do you understand by the statement that an organic compound is optically active? Explain the relation between optical activity and stereoisomerism by taking the example of tartaric acid. (*Rajasthan, B.Sc., 1962*)

18. Write a short note on Resolution of Racemic compounds. (*Lucknow, B.Sc., 1960*)

19. What do you understand by Optical Activity? What is the difference between racemic and mesotartaric acid? Give the projection formulae of *d*- and *l*-lactic acids? (*Lucknow, B.Sc., 1962*)

20. Write a short note on *Cis*-trans Isomerism. (*Lucknow, B.Sc., 1959, 1961*)

21. Give an account of the asymmetric organic compounds containing (*i*) nitrogen and (*ii*) sulphur. (*Bombay, B.Sc., 1944*),

22. Give an account of the compounds of carbon showing optical activity due to molecular asymmetry. (*Bombay, B.Sc., 1950*)

23. Give an account of optically active compounds of carbon which do not contain an asymmetric carbon atom. Show how the optical activity of such compounds has been accounted for. (*Bombay, B.Sc., 1950, 1953*)

24. Give a short account of the stereochemistry of organic compounds of nitrogen. (*Bombay, B.Sc., 1958*)

25. Describe any two methods for achieving Asymmetric Synthesis? (*Bombay, B.Sc., 1959*)

26. Give an account of the isomerism of lactic and tartaric acids. (*Agra, B.Sc., 1960*)

27. Write an account of Geometrical Isomerism, mentioning typical compounds which show this kind of isomerism. How can the configuration of a given isomeride be determined? (*Punjab, B.Sc., 1963*)

CHAPTER EIGHT

CATALYTIC ORGANIC REACTIONS

1. For a general discussion of the phenomenon of catalysis, characteristics of a catalytic action, and theories of catalysis, the reader is referred to a text-book of general chemistry[1]. We shall here take up the applications of catalysis in various organic reactions :—

(1) **Oxidation.** Most of the primary and secondary alcohols readily lose hydrogen when heated in contact with a catalyst. Thus, ethyl alcohol gives an 80 per cent yield of acetaldehyde when passed over zinc heated at 660° :

$$CH_3.CH_2OH \rightleftharpoons CH_3.CHO + H_2$$

Isopropyl alcohol gives an almost quantitative yield of acetone when its vapour is passed over reduced copper heated at 250° to 320°C :

$$CH_3.CHOH.CH_3 \rightleftharpoons CH_3.CO.CH_3 + H_2$$

The oxidation of methyl alcohol to formaldehyde by air in the presence of finely-divided platinum is another familiar example. An oxidation reaction of commercial importance is the conversion of naphthalene into phthalic acid by fuming sulphuric acid in the presence of metallic mercury or mercuric sulphate, or by air in the presence of vanadium pentoxide. In Kjeldahl's method for the estimation of nitrogen (chap. 3, sec. 5) the addition of a catalyst (mercury, mercuric oxide, cupric sulphate or manganese dioxide) greatly facilitates the oxidation.

An important catalytic oxidation of biological importance was discovered by Fenton, who showed that hydrogen peroxide, in the presence of a small quantity of ferrous sulphate as catalyst, brings about the oxidation of certain organic compounds ; *e.g.*,

$$\underset{\text{Lactic acid}}{CH_3.CH(OH).COOH} + H_2O_2 \longrightarrow \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + 2H_2O$$

(2) **Reduction.** Catalytic reduction, *i.e.*, reduction by means of hydrogen in the presence of finely-divided metals, was thoroughly investigated by *Sabatier* and *Senderens* in the years 1897 to 1911. Of the various metals tried, nickel was found to be the most efficient. It is absolutely necessary that the metal be in an extremely fine state of division. This is accomplished by heating the metallic oxide in a current of hydrogen at a temperature of about 300°.

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[1] See *e.g.*, "Textbook of Physical Chemistry", Chap. 19, N. Singh and J. Singh (Atma Ram & Sons, Delhi).

The method of catalytic reduction has been found to be of very wide application. The substance to be reduced is usually vaporized, mixed with excess of hydrogen, and passed over finely-divided nickel heated at 150°—250°.

Of the numerous reductions which have been effected by this process, the following few may be mentioned as examples:

(*a*) Ethylene to ethane :

$$C_2H_4 + H_2 \xrightarrow{\text{Ni at } 130^\circ-150^\circ} C_2H_6$$

(*b*) Allyl alcohol to *n*-propyl alcohol :

$$CH_2{=}CH.CH_2OH + H_2 \xrightarrow{\text{Ni at } 160^\circ-180^\circ} CH_3.CH_2.CH_2OH.$$

(*c*) Methyl isocyanide to dimethylamine :

$$CH_3NC + 2H_2 \xrightarrow{\text{Ni at } 160^\circ-180^\circ} CH_3.NH.CH_3$$

(*d*) Nitromethane to methylamine :

$$CH_3NO_2 + 3H_2 \longrightarrow CH_3NH_2 + 2H_2O$$

(*e*) Benzene and its homologues to cyclohexane and its homologues :

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$$

(*f*) The method of catalytic reduction is nowadays extensively employed on a commercial scale for the manufacture of *margarine* and *artificial ghee* by the hydrogenation of oils. The process consists in passing hydrogen through the heated oil in which finely-divided nickel has been suspended. The unsaturated liquid glycerides are thereby converted into the corresponding saturated compounds, which are solid fats :

$$\underset{\text{Olein}}{C_3H_5(O.COC_{17}H_{33})_3} + 3H_2 \longrightarrow \underset{\text{Strearin}}{C_3H_5(O.COC_{17}H_{35})_3}$$

Metals other than nickel are sometimes used in catalytic reduction by means of hydrogen. Thus *Rozenmund* in 1918 employed finely-divided platinum (or palladium) precipitated upon an inert material (such as $BaSO_4$) for the catalytic reduction of acid chlorides to aldehydes :

$$RCOCl + H_2 \longrightarrow RCHO + HCl$$

(3) **Dehydration.** Many organic substances containing hydrogen and oxygen lose the elements of water when their vapours are passed over heated aluminium oxide, phosphate or silicate. Thus, when ethyl alcohol is passed over aluminium oxide heated at about 400°, it yields ethylene :

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

Another example of catalytic dehydration is the conversion of an amide into nitrile when the vapour of the former is passed over aluminium heated to 420° :

$$\underset{\text{Acetamide}}{CH_3CONH_2} \longrightarrow \underset{\text{Acetonitrile}}{CH_3CN} + H_2O$$

(4) **Alkylation of Ammonia.** See chap. 26, sec. 2.

(5) **Estrification.** *Sabatier* and *Maihle* have shown that when a mixture of molecular proportions of an alcohol and an acid in the

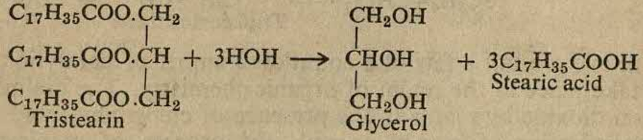
vapourous state is passed over a column of titanium dioxide kept at 290°—300°, a 70 per cent yield of the ester is obtained. The process has been found to be extremely rapid.

(6) **Hydrolysis.** The following cases exemplify the hydrolytic decomposition of organic substances under the influence of catalysts :—

(*a*) Hydrolysis of an ester in the presence of a mineral acid or an alkali :

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

(*b*) Hydrolysis of fats and oils by superheated steam in the presence of a little lime :



$$\underset{\text{Tristearin}}{\begin{array}{l} C_{17}H_{35}COO.CH_2 \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO.CH \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO.CH_2 \end{array}} + 3HOH \longrightarrow \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH}$$

One of the methods for effecting the hydrolysis of fats and oils is by means of the Twitchel reagent (sulpho-benzene-stearic acid).

(*c*) Hydrolysis of acid amides and acid nitriles in the presence of mineral acids or aqueous alkalies :

$$\underset{\text{Acetamide}}{CH_3CONH_2} + HOH \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

$$\underset{\text{Acetonitrile}}{CH_3C{\equiv}N} + 2H_2O \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(7) **Friedel and Crafts' Reaction.** This is a very important catalytic reaction in which anhydrous aluminium chloride is used as a catalyst. It is employed for the preparation of homologues of benzene and certain other aromatic compounds. The following are the more important examples of the use of this reaction :

(*a*) When a benzene hydrocarbon is treated with an alkyl halide in the presence of anhydrous aluminium chloride, the alkyl group enters the benzene ring ; *e.g.*,

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5{\cdot}CH_3} + HCl$$

$$C_6H_6 + 2CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Xylene}}{C_6H_4(CH_3)_2} + 2HCl$$

(*b*) When an acid chloride is added to a benzene hydrocarbon in the presence of anhydrous aluminium chloride, a ketone results ; *e.g.*,

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

(*c*) When a benzene hydrocarbon is treated with phosgene gas, in the presence of anhydrous aluminium chloride, an acid chloride is produced,

$$\underset{\text{Benzene}}{C_6H_6} + COCl_2 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

The acid chloride, on being decomposed with water, gives a carboxylic acid :

$$C_6H_5COCl + H_2O \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$$

(*d*) Formation of *diphenylmethane*, by the interaction of methylene chloride and benzene, and of *triphenylmethane*, by the interaction of chloroform and benzene, are other examples of Friedel and Crafts' reaction :

$$C_6H_6 + CH_2Cl_2 + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + 2HCl$$

$$3C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} \underset{\text{Triphenylmethane}}{(C_6H_5)_3CH} + 3HCl$$

The above are but a few of a countless number of catalytic reactions that take place in the realm of organic chemistry. The assimilation of carbon dioxide by plants in the presence of chlorophyl and sunlight, the assimilation of food by animals, the process of respiration, and numerous other anabolic and catabolic changes taking place in plants and animals are all catalytic in nature. Numerous other examples of catalytic organic reactions will be met with in the following chapters.

2. Enzyme Catalysis.—The most important class of heterogeneous catalytic reactions occurring in aqueous solution is that of enzyme reactions. **Enzymes** are of natural origin, being produced in living cells of animals and plants. Chemically, they all belong to the class of organic substances called *proteins*. They consist, therefore, of macromolecules having, in each case, a definite chemical constitution and configuration.

Classification of Nomenclature of Enzymes.—

Enzymes are classified according to the type of reactions they catalyse. Accordingly, they are grouped as **hydrolases, oxidases, reductases**, etc. The names of specific enzymes all end in *—ase*, and are usually derived from the substances upon which they act. Thus, the enzyme that brings about the hydrolysis of maltose is called *maltase*, and the one that decomposes sucrose (cane or beet sugar) into glucose and fructose is called *sucrase*. Sometimes, the name may be derived from the reaction that is being catalysed. Thus *sucrase* is also called *invertase*, as it brings about the "inversion" of sucrose.

Fig. 1. Yeast cells (highly magnified).

Some Examples of Enzyme Action.—

The simplest example of fermentation is that of sugar by yeast to form ethyl alcohol, C_2H_5OH. The yeast cells (Fig. 1) contain, a number of enzymes, two of which, called **invertase** and **zymase**, are concerned in the alcoholic fermentation of sugar. The invertase first causes the hydrolytic decomposition of cane-sugar into glucose and fructose, which are then decomposed by zymase to form alcohol and carbon dioxide.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}G_6}$$

$$C_6H_{12}O_6 \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Another familiar example is the **lactic fermentation** of milk. When a small quantity of curd (*jag*) is added to warm milk, the sugar present in the milk is converted into lactic acid by a certain species of bacteria, called **lactic bacillus.** The lactic acid causes the coagulation of the albumen present in the milk, producing the curd. On keeping, the curd goes sour, because the lactic acid it contains is converted into butyric acid by the action of another ferment called **butyric bacillus.** The optimum temperature for the lactic fermentation is 34° to 35°C; hence the necessity of adding the ferment to warm milk.

Enzymes play an important role in digestive processes and in food chemistry. During mastication of food, starch is converted partially into hexoses by the action of **ptyalin** present in saliva. Excretion of various glands in the stomach contain enzymes and all reactions that take place during the digestion of food are enzymic actions.

A number of other examples of fermentation will be dealt with at their proper places.

Characteristics of Enzyme Action.—

The following are the more important characteristics of enzyme action :—

(1) Each enzyme is specific for a given reaction. Thus, *urease* catalyses the hydrolysis of urea, NH_2CONH_2, but has no effect on the rate of hydrolysis of methylurea, $NH_2.CO.NH(CH_3)$. Perhaps the most striking example of the specific action of enzymes is that of hydrolysis of α- and β- glucosides. The former are hydrolysed by *maltase* but not by *emulsin,* while the reverse is true of the β-isomers.

(2) In the case of reversible processes, the enzymes, like other catalysts, are able to catalyse both the forward and the backward reactions, the point of equilibrium remaining unaffected.

(3) Enzymes resemble colloidal metals in being readily poisoned by traces of the same substances that poison the latter.

(4) The rate of an enzyme reaction depends upon conditions of temperature, concentration and pH. Being negligible in the 0° range, the enzyme activity rises rapidly with temperature up to a point, called the *optimum temperature.* This point of maximum activity varies with different enzymes, but lies usually between 35° and 50°. Beyond the optimum temperature, the enzyme activity begins to be adversely affected, and most enzymes get utterly inactivated or destroyed at about 70°.

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Nature of Enzyme Catalysis.—

One of the earliest processes of enzyme catalysis is the fermentation of sugar by yeast to produce ethyl alcohol and carbon dioxide. Pasteur, who carried out exhaustive research in this field, held the view that fermentation is a purely physiological action, dependent upon the life processes of the yeast cells. Liebig, on the other hand, regarded the phenomenon as of purely chemical nature.

H. Bucbner (1897), with a view to settling the controversy between the physiological and the chemical view-points, submitted yeast to strong pressure, thereby disrupting the cell walls and obtaining an aqueous extract. This was filtered in order to free it completely from the adhering cells. The "expressed yeast juice", thus obtained, was found to set up fermentation quite as well as the living yeast itself. He came to the conclusion that the yeast cells contained non-living, chemical substances capable of bringing about fermentation. These he called **enzymes.** The part played by the yeast cells in bringing about fermentation of sugar, therefore, is an indirect one—that of producing the "enzymes", which are the real catalysts for the fermentation reactions.

Enzyme catalysis may appear to be homogeneous at first sight. But, in reality, it is *heterogeneous*, as the enzyme being colloidal in nature, forms a separate phase from the true solution of the substance undergoing reaction. By the way, it may be mentioned that the reacting substance in enzyme catalysis is given the name of "**substrate**" by enzyme chemists.

Kinetics of Enzyme Catalysis.—

Experimentally, it has been found that the rate of an enzyme-catalysed reaction varies with the concentration of substrate as well as that of the enzyme, The reaction, therefore, is of the second order. If the concentration of the substrate is kept constant and the rate of reaction determined at different initial concentrations of the enzyme, the rate of reaction is proportional to the enzyme concentration (Fig. 2). That is, the reaction is then of the first order.

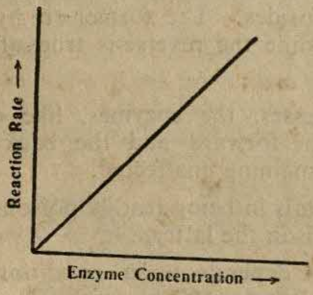


Fig. 2. Variation of reaction rate with enzyme concentration, the substrate concentration being kept constant.

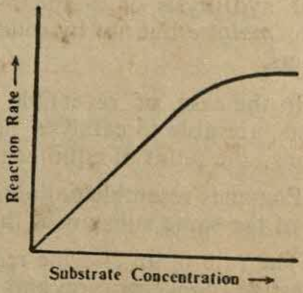


Fig. 3. Variation of reaction rate with substrate concentration, the enzyme concentration being kept constant.

On the other hand, if the concentration of the enzyme is kept constant and the substrate concentration varied, the reaction-rate curve assumes the form shown in Fig. 3. In this case, the rate is proportional to the concentration of the substrate so long as this concentration is small. At high concentrations, however, the reaction rate becomes independent of the concentration. The reaction is then of the **zero order.** This state of affairs is realized when such parts of enzyme macromolecule, as are catalytically active have been completely covered with the substrate molecules. The behaviour is similar to that of some homogeneous gas reactions occurring on solid surfaces.

QUESTIONS

1. Give an account of the use of catalytic agents in organic chemistry. (*Punjab, B.Sc., 1921*)

2. What do you know of *fermentation processes*? Name any six organic compounds which are produced by this process, and describe the manufacture by fermentation of any *one* of them. (*Punjab, B.Sc., 1926*)

3. Write notes on : (*i*) Catalytic reduction, (*ii*) Friedel and Crafts reaction and (*iii*) Enzyme action.

4. Write a note on "Fermentation and its Applications". (*Punjab, B.Sc., 1941*)

5. Explain the catalytic nature of enzymes and their action. (*Bombay, B.Sc., 1955*)

6. Write an essay on Enzymes and their action. (*Bombay, B.Sc., 1958*)

7. What is a catalyst ? What are the conditions a substance must satisfy in order to be considered a catalyst ? Describe two industrially important catalytic processes. (*Kerala, B.Sc., 1957 ; Travancore, B.Sc., 1957*)

8. What are the characteristics of a catalyst ? On the basis of the theory of contact catalysis, explain :

   (*a*) the action of catalytic poisons ;
   (*b*) the specific nature of a catalyst ;
   (*c*) the activity of finely-divided catalysts. (*Agra, B.Sc., 1959*)

9. What is meant by the term 'catalysis' ? What criteria have been laid down for catalyst behaviour ? Discuss the applications of catalysis in industry. (*Banaras, B.Sc., 1950*)

10. What criteria would you apply to show that a particular substance taking part in a reaction is not a reactant but a catalyst ? What theories have been advanced to explain the phenomenon of catalysis ? (*Agra, B.Sc., 1956*)

CHAPTER NINE

ALKANES

1. Aliphatic Compounds.—The numerous substances classified as *aliphatic* or *fatty* compounds (also called *open-chain* or *acyclic* compounds) may be regarded as derived from methane, CH_4, the first member of the homologous series of saturated hydrocarbons dealt with in this chapter. The name "aliphatic" refers to the inclusion in this group of the animal and vegetable fats.[1] In respect of molecular constitution, the compounds of this class are distinguished by their having *open* carbon chains in contrast to the closed carbon chains or rings of the "aromatic" series.

2. Alkanes.—The methane-ethane series of hydrocarbons are called **saturated hydrocarbons**, as in their molecules the carbon valencies are fully saturated with hydrogen. Another name sometimes applied to this series is **paraffin hydrocarbons**, which is based on the fact that these hydrocarbons are characteristically inert towards many reagents (L. *parum*, little and *affinis*, affinity). The modern systematic designation of this series is **alkanes.**

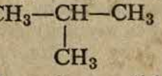
The **general formula** of the alkanes is C_nH_{2n+2}.

3. Isomerism in Alkanes.—As we have seen in chapter 5 (sec. 2), there are two postulates of the theory of structure of organic molecules : (*i*) tetracovalency of carbon, and (*ii*) formation of carbon chains. On the basis of these two postulates, we can predict the number of possible isomers in the case of any given alkane.

Two Butanes. In this way, we were able to show (*see* chap. 5, sec. 4) that while there could exist only one isomer in the case of methane, ethane and of propane, the next member, *i.e.*, **butane** C_4H_{10}, can exist in the following *two* forms :—

(*i*) $CH_3-CH_2-CH_2-CH_3$ *normal* Butane

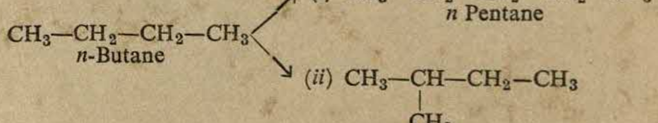
(*ii*)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ *iso*-Butane

No third form is possible here.

Three Pentanes. From normal butane it is possible to derive two pentanes as shown below :—



(*i*) $CH_3-CH_2-CH_2-CH_2-CH_3$
n Pentane
$CH_3-CH_2-CH_2-CH_3$
n-Butane
(*ii*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

2-Methylbutane (*isopentane*)

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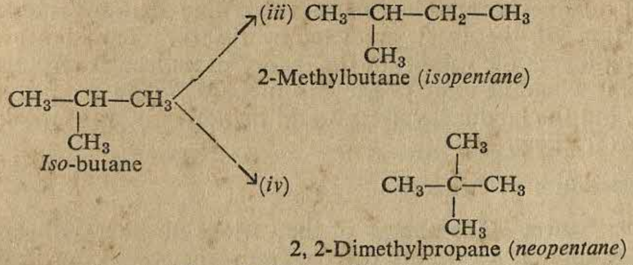
[1] Greek : *Aliphos*, fat.

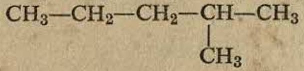
Similarly, from isobutane we can have two possible pentanes :—

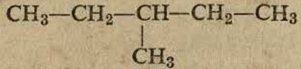

(iii) CH₃—CH—CH₂—CH₃
CH₃
2-Methylbutane (isopentane)
CH₃—CH—CH₃
CH₃
Iso-butane
(iv)
CH₃—C—CH₃
2, 2-Dimethylpropane (neopentane)

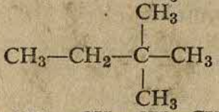
Since structures (*ii*) and (*iii*) are identical there can exist, according to theory, only *three* pentanes.

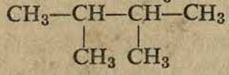
Five Hexanes. Similarly, from the three pentanes we can derive *five* possible hexane structures :—

(*i*) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ *n*-Hexane

(*ii*)

$CH_3{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$
2-Methylpentane

(*iii*)

$CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3$
3-Methylpentane

(*iv*)

$CH_3{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3$
2, 2-Dimethylbutane

(*v*)

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$
2, 3-Dimethylbutane

Hence, from the theory of structure it follows that there can exist *two* butanes, *three* pentanes and *five* hexanes. The number of isomers actually prepared in these, and a large number of other cases, is *always in agreement* with what the theory predicts. This constitutes the **strongest support for the theory of molecular structure** discussed in Chapter 5.

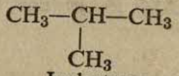
The number of possible structural isomers rises rather too steeply with the increase of carbon atoms in the alkane molecule, as will appear from the following table :—

Alkane	*Number of isomers*	*Alkane*	*Number of isomers*
CH_4	1	C_8H_{18}	18
C_2H_6	1	C_9H_{20}	35
C_3H_8	1	$C_{10}H_{22}$	75
C_4H_{10}	2	$C_{15}H_{32}$	4 347
C_5H_{12}	3	$C_{20}H_{42}$	366,319
C_6H_{14}	5	$C_{40}H_{82}$	62,491,178,805,831
C_7H_{16}	9		

Needless to say that the number of isomers actually isolated in the case of alkanes containing more than nine carbons is a very minute fraction of the total predicted by theory. This, however, in no way minimizes the validity of the theory of molecular structure. In principle, it would be quite possible to prepare *all* the isomers in such a case, but the labour involved would be not only too tremendous but also fruitless.

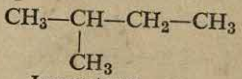
4. Nomenclature of Alkanes—

(1) **Common System.** The names of the various members of series all end in **-ane**, and, as a rule, are derived from the Greek or Latin numerals indicating the number of carbon atoms in the molecule. The first four members of the series, however, possess special names. Alkanes having *all* the carbon atoms linked in a straight chain are called **normal** (abbreviated *n*-, as in *n*-butane, *n*-pentane, etc.). As to the branched-chain hydrocarbons, it is customary to use the prefix **iso** for structures having the branching of *one* carbon atom at the *end* of the chain, as in isobutane and isopentane :



$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$

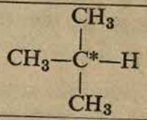
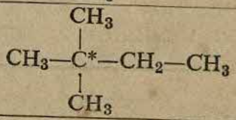
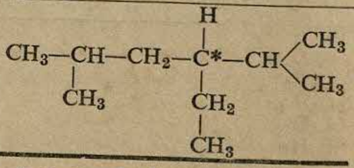
Isobutane



$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_3$

Isopentane

The nomenclature of more complex, branched-chain alkanes, is based on the fact that any member of the homologous series may be regarded as a **derivative of methane.** For this purpose, the *most highly branched* carbon atom is taken as the methane carbon atom and the various alkyl groups linked with it are named **in order of increasing size.** The following examples illustrate this method of nomenclature, the "methane carbon atom" being in each case marked with an asterisk* for the sake of clearness :—

Name	*Structure*
1. Trimethylmethane	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C^*}}-H$
2. Trimethyl-ethylmethane	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C^*}}-CH_2-CH_3$
3. Ethyl-isopropyl-isobutylmethane	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-\overset{\overset{H}{\vert}}{\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{C^*}}-CH\begin{matrix}CH_3\\CH_3\end{matrix}$

This method of naming branched-chain hydrocarbons fails if the alkyl group possesses neither a normal nor an *iso*-structure. A second and more elaborate method of nomenclature which does not suffer from this defect is described below.

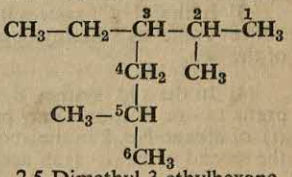
(2) **Geneva or I.U.C. System.** A comprehensive scheme of nomenclature of organic compounds was evolved by the international congress of leading chemists held in Geneva (Switzerland) in 1892. This system, known as the **Geneva System**, was modified and extended by the **International Union of Pure and Applied Chemistry** (**I.U.P.A.C.** or simply **I.U.C.**), which first met at Liege (Belgium) in 1930 and then at Amsterdam (Holland) in 1949.[1] The revised rules, so far as they apply to alkanes, may be summed up as under :—

(1) Locate the **longest possible chain** of carbon atoms, and name the compound as a derivative of this *n*-alkane.

(2) Number the carbon atoms of the chain so that the **sum of the numerals** *used to indicate the positions of the side-chains is the* **minimum.**

(3) Name and locate the various side chains by the numerals assigned to the carbon atoms carrying these chains. In naming the alkyl groups constituting the side chains the prefixes *n*- and *iso*- are not permissible. Further, the names of the substituent alkyl groups are arranged in **alphabetical order** and the *compound name* of a substituent is treated as a unit with its own alphabetic position ; thus *dimethyl* precedes *ethyl* but follows *amyl.*

We may illustrate the system by reference to the formula given in the margin. The first point to note is that the longest chain is *not* the pentane chain, as might appear at first sight, but the hexane system extending from one end of the chain through the butyl group. The second point is that the numbering of the carbon atoms of the selected chain must be done in such a way that the **sum of the numerals** defining the positions of the side chains must be the **minimum.** If the carbon atoms of the hexane chain are numbered as shown in the above scheme, the name of the hydrocarbon works out to be **2,5-dimethyl-3-ethylhexane**, the sum of the numerals being 10. If, on the other hand, the numbering be done in the reverse order, the name of the hydrocarbon would be 2,5-dimethyl-4-ethylhexane. The sum of the numerals employed in that case would be 11 ; that is, it would be higher than that obtained with the first alternative. Hence, the first name is the correct one and *not* the second. A third point to be noted in this case is that it is possible to select another hexane chain as the reference structure by numbering the carbon atoms starting from the *bottom* of the formula and ending at the extreme *left*. In that case, the name of the hydrocarbon would be 2-methyl-4-isopropylhexane, which again is incorrect, as the prefix *iso*- must not appear in the IUC names.



2,5-Dimethyl-3-ethylhexane

From the foregoing discussion it is clear that the restrictions indicated above give rise to a **uniform system of nomenclature.**

The Table on the next page summarizes the common and the I.U.C. names for the two butanes and the three pentanes.

Notes on the Table.

(1) The prefix **iso-** is properly used only for compounds containing $(CH_3)_2CH$— group.

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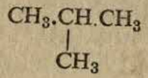
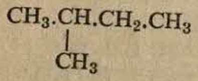
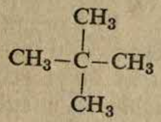
[1] The names and rules adopted by the I.U.P.A.C. in its former sessions were confirmed at 16th Conference in New York City in 1951 with slight modifications.

Formula	*Common name*	*I.U.C. or Geneva name*
(1) $CH_3.CH_2.CH_2.CH_3$	*n*-Butane	Butane
(2)  $CH_3.\underset{\underset{\displaystyle CH_3}{\vert}}{CH}.CH_3$	(*i*) Isobutane or (*ii*) Trimethylmethane	2-Methylpropane
(3) $CH_3.CH_2.CH_2.CH_2.CH_3$	*n*-Pentane	Pentane
(4)  $CH_3.\underset{\underset{\displaystyle CH_3}{\vert}}{CH}.CH_2.CH_3$	(*i*) Isopentane or (*ii*) Dimethylethylmethane	2-Methylbutane
(5)  $CH_3-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-CH_3$	(*i*) Neopentane or (*ii*) Tetramethyl methane	2, 2-Dimethylpropane

(2) The prefix **neo-** indicates the presence of a carbon atom attached by all its four valencies to other carbon atoms.

(3) In the I.U.C. system it is not permissible to name alkane No. 4 in the above Table as 3-Methylbutane, as the numeral to be used must be the *smaller* of the two.

(4) In the old system a branched-chain alkane may be designated by the prefix *iso-* or *neo*, or it may be regarded as a derivate of methane The first name (*i*) of alkane No. 2 in the above table is in accordance with the first system and the second name (*ii*) is in accordance with the second system.

5. Occurrence of Alkanes in Nature.—Alkanes occur in nature in tremendous quantities, the chief source being **mineral oil** or **petroleum**, which occurs in many parts of the world. Methane, the first member of the series, is found as **marsh gas** and **fire-damp**. It is also the chief constituent of coal-gas and natural gas. Besides petroleum, **natural gas, shale** and **ozokerite** are the most important commercial sources of alkanes.

6. Isolation, Preparation and Formation of Alkanes.—

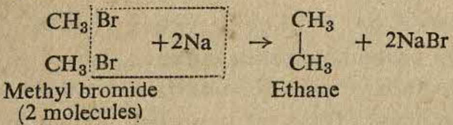
(1) **Isolation from Natural Sources.**—Methane, ethane, propane, butane and isobutane are isolated from natural gas and the gasoline fraction of petroleum distillation by fractional condensation and repeated fractionation. These sources have acquired considerable importance in recent years in connection with the production of aviation gasoline (alkylate) and petrochemicals.

(2) **Synthesis from Carbon and its Simpler Compounds.** Syntheses of methane from carbon, carbon monoxide, carbon disulphide and aluminium carbide (see sec. 8) are of considerable theoretical interest,

as they afford means of preparing in the laboratory organic substances from inorganic materials. Such syntheses were responsible for the overthrow of the "vital force theory", and thus opened up the vast field of organic chemistry for investigation and exploitation.

The production of synthetic petrol from coal (Bergius process) and from water gas (Fischer-Tropsch process), described in a later chapter, are examples of the application of simple syntheses to the solving of problems of great industrial importance.

(3) **Wurtz Synthesis (Building-up of carbon chains).** When methyl bromide (or iodide) in ethereal solution is treated with metallic sodium, we get *ethane* :



$$\begin{matrix} CH_3Br \\ CH_3Br \end{matrix} + 2Na \rightarrow \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2NaBr$$

Methyl bromide (2 molecules) Ethane

Similarly, ethyl bromide, C_2H_5Br, gives *butane*, C_4H_{10} ; propyl bromide, C_3H_7Br, yields *hexane*, C_6H_{14} ; and butyl bromide, C_6H_9Br, yields *octane*, C_8H_{18}. As a final example of this remarkable reaction, it may be mentioned that the hydrocarbon $C_{60}H_{122}$ has been obtained from $C_{30}H_{61}Br$ by the action of sodium.

Wurtz synthesis, though primarily useful for preparing alkanes with an *even* number of carbon atoms may be used to synthesize alkanes with *odd* number of carbon atoms. Thus, when a mixture of methyl and ethyl iodides is submitted to Wurtz reaction, we get propane, C_3H_8, admixed with approximately equal amounts of ethane and butane. Since it is not ordinarily possible to separate such a mixture of gases in the laboratory, the method is of little practical importance.

Wurtz synthesis, as we have just seen, is of great importance in **building up higher hydrocarbons** from the lower members.

(4) **Kolbe's Reaction— another method of building-up carbon chains.** When concentrated aqueous solutions of sodium salts of fatty acids are submitted to electrolysis, we get an alkane containing *double the number of carbon atoms present in the alkyl group component of the acid molecule ; e.g.*,

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$\underset{\text{Acetate ion}}{2CH_3COO^-} \xrightarrow[-2e^-]{\text{anodic oxidation}} \underset{\text{Ethane}}{CH_3.CH_3} + 2CO_2$$

The reaction consists in the **oxidation of the anion** at the anode, so that a mixture of alkane and carbon dioxide is evolved at the anode.[1]

If a mixture of two salts be used, we get a mixture of three alkanes. Thus, a mixture of sodium acetate and sodium propionate would give a mixture of ethane, propane and butane.

---

[1] At the cathode, *reduction* of water occurs with generation of hydrogen and alkali :

$$2Na^+ + 2H_2O + 2e^- \rightarrow 2NaOH + H_2$$

This reaction, in effect, is analogous to Wurtz' synthesis, but is much restricted in application.

(5) **Degradation of Carbon Chains.** Methods 2, 3 and 4 involve building-up of carbon chains. Conversely, longer chains can be broken down to shorter ones as follows :—

(*i*) **Duma's method of decarboxylation of fatty acids.** When anhydrous sodium (or potassium) salt of a fatty acid is heated with soda-lime, we get the alkane containing **one carbon atom less** than the one from which the fatty acid was derived. Thus, a mixture of the sodium salt of acetic acid (a derivative of *ethane*) and soda-lime, on dry-heating, evolves *methane* :

$$CH_3\boxed{COONa + NaO}H \rightarrow CH_4 + Na_2CO_3$$

Similarly, sodium propionate yields ethane :—

$$C_2H_5COONa + NaOH \rightarrow C_2H_6 + Na_2CO_3$$

(*ii*) **Cracking or Pyrolysis.** This very important method of converting hydrocarbons into lower ones is discussed later under "Reactions of Alkanes", and is of great practical importance in the manufacture of gasoline and oil gas.

(6) **Reduction of alkyl halides with nascent hydrogen.** When an alkyl halide is treated with zinc-copper couple and alcohol, or tin and hydrochloric acid, or hydriodic acid and red phosphorus, it gets reduced to the corresponding alkane :—

$$\underset{\text{Methyl iodide}}{CH_3I} + 2H \rightarrow \underset{\text{Methane}}{CH_4} + HI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \rightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(7) **Reduction of alcohols.** A modification of the above method is the reduction of an alcohol instead of the alkyl halide with **hydriodic acid and red phosphorus.** The hydriodic acid first converts the alcohol into alkyl iodide and then reduces the latter to an alkane :—

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HI \xrightarrow{\text{Esterification}} \underset{\text{Ethyl iodide}}{C_2H_5I} + H_2O$$

$$C_2H_5I + HI \xrightarrow{\text{Reduction}} \underset{\text{Ethane}}{C_2H_6} + I_2$$

Note. A mixture of hydriodic acid and red phosphorus is much used in organic chemistry as a **strong reducing agent.** The function of red phosphorus is to regenerate hydriodic acid by combining with iodine produced in the reaction. The phosphorus triiodide thus produced reacts with the water present in the acid to regenerate hydriodic acid :—

$$2P + 3I_2 \rightarrow 2PI_3$$

$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

(8) **Reduction of fatty acids.** Reduction of fatty acids, more particularly the higher ones, affords a valuable method for the preparation of alkanes. The reduction is carried out with hydriodic acid and red phosphorus.

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + 6HI \rightarrow \underset{\text{Octadecane } (C_{18}H_{38})}{C_{17}H_{35}CH_3} + 2H_2O + 3I_2$$

(9) **Hydrogenation of unsaturated hydrocarbons—Sabatier and Senderens Reaction.** When a mixture of hydrogen and an unsaturated hydrocarbon is passed over finely divided platinum or nickel at a high temperature, the unsaturated hydrocarbon is hydrogenated to an alkane :—

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + H_2 \rightarrow \underset{\text{Ethane}}{H_3C{-}CH_3}$$

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + 2H_2 \rightarrow \underset{\text{Ethane}}{H_3C{-}CH_3}$$

The method is an important one, as certain unsaturated hydrocarbons, such as ethylene and acetylene, are readily available substances.

(10) **From an Alkyl Halide through Grignard's Reaction.** One method of preparing an alkane from an alkyl halide, *i.e.*, by reduction, has already been described. An alternative method consists in treating the alkyl halide with dry magnesium in the presence of dry ether (Grignard's reaction), and decomposing the product (called a **Grignard's reagent**), with water :—

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + Mg \rightarrow \underset{\substack{\text{Ethyl-magnesium}\\ \text{iodide}}}{C_2H_5MgI}$$

$$C_2H_5MgI + HOH \rightarrow \underset{\text{Ethane}}{C_2H_6} + Mg(OH)I$$

7. Physical Properties of Alkanes.—

(*i*) The first four members of this series are colourless gases, the next 11 (*i.e.*, from C_5H_{12} to $C_{15}H_{32}$) are volatile liquids, while the higher ones (*i.e.*, from $C_{16}H_{34}$ onwards) are colourless, waxy solids.

The following table summarizes the boiling points, the melting points and the specific gravities (as liquids) of the first 18 *normal* alkanes :—

Name	*Formula*	*M.P., °C*	*B.P., °C*	*Sp. Gr. (as liquid)*
Methane	CH_4	−182·44°	−161·5°	0·436 at −170°C
Ethane	$CH_3.CH_3$	−183·27	− 88·63	0·548 ,, −90
Propane	$CH_3.CH_2CH_3$	−187·69	− 42·07	0·5780 ,, −40
n-Butane	$CH_3(CH_2)_2CH_3$	−138·35	− 0·50	0·6116 ,, −10
n-Pentane	$CH_3(CH_2)_3CH_3$	−129·72	+ 36·07	0·6263 ,, +20°C
n-Hexane	$CH_3(CH_2)_4CH_3$	− 95·34	+ 68·74	0·6594
n-Heptane	$CH_3(CH_2)_5CH_3$	− 90·601	+ 98·43	0·6838 ,, ,,
n-Octane	$CH_3(CH_2)_6CH_3$	− 56·80	+125·67	0·7025 ,, ,,
n-Nonane	$CH_3(CH_2)_7CH_3$	− 53·54	+150·80	0·7176 ,, ,,
n-Decane	$CH_3(CH_2)_8CH_3$	− 29·67	+174·12	0·7301 ,, ,,
n-Undecane	$CH_3(CH_2)_9CH_3$	− 25·60	+195·88	0·7402 ,, ,,
n-Dodecane	$CH_3(CH_2)_{10}CH_3$	− 9·6	+216·3	0·7493 ,, ,,
n-Tridecane	$CH_3(CH_2)_{11}CH_3$	− 6	+230	0·7568 ,, ,,
n-Tetradecane	$CH_3(CH_2)_{12}CH_3$	+ 5·5	+251	0·7636 ,, ,,
n-Pentadecane	$CH_3(CH_2)_{13}CH_3$	+ 10	+268	0·7688 ,, ,,
n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	+ 18·15	+287·05	0·7733 ,, ,,
n-Heptadecane	$CH_3(CH_2)_{15}CH_3$	+ 22·0	+303	0·7767 at +25°
n-Octadecane	$CH_3(CH_2)_{16}CH_3$	+ 28·0	+317·38	0·7750 at +30°

(*ii*) From the above table, we see that the **boiling points** rise with the increase in the size of the molecule. The increase, however, becomes smaller and smaller, as the series is ascended. Thus, while the difference between the boiling points of CH_4 and C_2H_6 is about 70°, it is only 20° in the case of $C_{11}H_{24}$ and $C_{12}H_{26}$.

For isomeric hydrocarbons, we may make the following statements as regards boiling points :—

(*a*) *The longer the chain, the higher the boiling point.*

(*b*) *For the same length of chain, the nearer the substituents to the middle of the chain, the higher the boiling point.*

(*iii*) The **melting points** also increase with the rise in the molecular weight.

(*iv*) The **specific gravities** of the liquid and solid alkanes increase but slowly with rising molecular weight. The higher members with the normal structure possess an almost constant specific gravity (from 0·776 to 0·780).

(*v*) As to **smell**, the gaseous members are practically odourless. The lower liquid members that are volatile possess the characteristic petrol-like odour. The highest members, that are colourless waxy solids, are non-volatile and, therefore, odourless.

(*iv*) Alkanes are practically completely immiscible in water. They are soluble in alcohol, ether and other organic solvents.

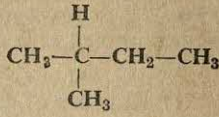
8. Reactions of Alkanes.—The alkanes, especially the straight-chain members of the series, are resistant to attack by powerful chemical reagents, such as concentrated sulphuric acid, boiling nitric acid, fused alkalis, potassium dichromate or permanganate. Because of this lack of chemical reactivity, the hydrocarbons of this series are often referred to as **paraffins** (Latin *parum*, little, and *affinis*, affinity).

It must not, however, be supposed that alkanes are altogether devoid of chemical reactivity. In fact, they undergo important chemical reactions, if conditions are made sufficiently severe. High temperatures and pressures and use of catalysts have been found to be very favourable factors for those reactions of alkanes that do not proceed under ordinary conditions. The more important reactions of alkanes are :

(1) **Halogenation.** The halogenation of alkanes can be brought about by heat, light or catalysis. Chlorination and bromination occur readily, but iodination takes place with difficulty. It is chlorination alone that is of appreciable commercial significance, and has been studied more thoroughly. When chlorine is used in excess, a mixture of all the possible monochloroderivatives is obtained, but the proportion of each is different. This was shown by Markownikoff (1875) to be due to the **difference of reactivity of primary, secondary and tertiary hydrogen atoms**, the reactivity being in the order :

Tertary > Secondary > Primary

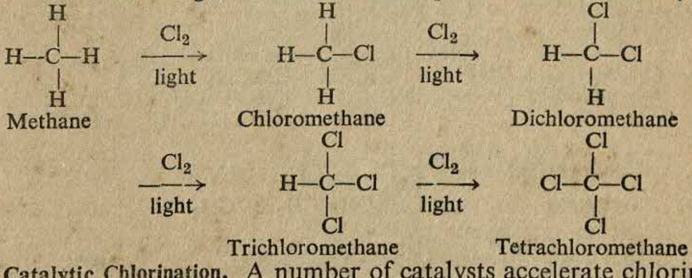
The above rule may be illustrated by reference to isopentane, or 2-methylbutane, the formula of which is given in the margin. The **"tertiary" hydrogen atom** attached to carbon No. 2 **is more reactive** and is the first to be replaced; the **"secondary" hydrogen atom of CH_2 groups** come next, and both of them get replaced after the tertiary one has reacted. Last of all, the hydrogen atoms of the terminal CH_3 groups called **"primary"** hydrogen atoms, are replaced, that is if there is a sufficient amount of chlorine present.



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_3$$

(*i*) **Thermal Chlorination.** Thermal chlorination of alkanes begins at 200°, and maximum yields are obtainable at about 300°. At higher temperatures, the reaction is complicated by pyrolysis of the alkane molecule. Controlled chlorination at the optimum temperature yields chiefly the monochloro-derivatives in accord with the Markownikoff rule given above. As the temperature is gradually raised, the reactivity of the primary, secondary and tertiary hydrogen atoms tends to become equal.

(*ii*) **Photochlorination.** The reaction between an alkane and chlorine (or bromine) occurs at the ordinary temperature in the presence of sunlight or artificial (ultraviolet) light. The reaction involves progressive chlorination, tending to be explosive. The **photochlorination of methane** gives a mixture of products. The reaction never stops at the initial stage, as the *primary reaction product is more reactive towards chlorine* than methane itself. The reaction mixture is always found to contain the di-, tri- and the tetrachloromethane, even though a considerable amount of unreacted methane is still present. The following reactions therefore proceed *simultaneously* :



(*iii*) **Catalytic Chlorination.** A number of catalysts accelerate chlorination. Cupric, ferric, antimonic and cerous chlorides are among the most effective catalysts for the purpose. Simultaneously reacting olefins act as promoters.

(*iv*) **Bromination.** The bromination of alkanes, though not so vigorous as chlorination, proceeds along the same lines, except that *not more than one bromine atom is taken up by each carbon atom* in the chain, even if there is an excess of bromine present. Thus, bromination of propane, $CH_3CH_2CH_3$, gives the following three products in the given order :—

$CH_3.CHBr.CH_3$	$CH_2Br.CHBr.CH_3$	$CH_2Br.CHBr.CH_2Br$
2-Bromopropane	1,2-Dibromopropane	1,2,3-Tribromopropane

(2) **Cracking or Pyrolysis.** The action of heat on alkanes, which is of considerable practical importance, results in the breaking up of the molecule into two or more fragments, and is termed *cracking, pyrolysis or thermal decomposition.* The total reaction is generally very complex and may involve the following types of decomposition :—

(*i*) Rupture of carbon-to-carbon linkages, resulting in the production of two or more small fragments.

(*ii*) Rupture of carbon-hydrogen bonds, resulting in the production of free hydrogen and one or more unsaturated hydrocarbons containing two or more double bonds.

(*iii*) Partial carbonization.

Cracking is conducted at temperatures varying from 400° to 700°C. It may be carried out at the atmospheric pressure (**vapour-phase cracking**) or under high pressures (**liquid phase cracking**). Two other modes of cracking, known as (**catalytic cracking** and **reforming**), are of considerable importance in the manufactures of synthetic gasolines, and will be discussed in that connection in chapter 11.

The following reactions are involved in the thermal decomposition of the hydrocarbons present in natural gas and natural gasolines :—

$$1.\quad \underset{\text{Methane}}{CH_4} \xrightarrow{1000^\circ} C + 2H_2$$

$$2.\quad \underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow{490^\circ} H_2C{=}CH_2 + H_2$$

$$3.\quad \underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow{460^\circ} \left\{\begin{array}{ll} CH_3{-}CH{=}CH_2 + H_2 & \qquad 45\% \\ CH_2{=}CH_2 + CH_4 & \qquad 55\% \end{array}\right.$$

$$4.\quad \underset{n\text{-Butane}}{CH_3.CH_2.CH_2.CH_3} \xrightarrow{430^\circ} \left\{\begin{array}{ll} \left.\begin{array}{l} CH_3.CH_2.CH{=}CH_2 + H_2 \\ CH_3.CH{=}CH.CH_3 + H_2 \end{array}\right] & 12\% \\ CH_3.CH{=}CH_2 + CH_4 & 50\% \\ CH_2{=}CH_2 + CH_3.CH_3 & 38\% \end{array}\right.$$

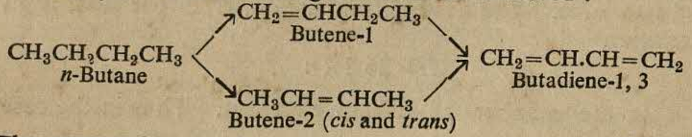
$$5.\quad \underset{\text{Isobutane}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\,CH_3} \xrightarrow{430^\circ} \left\{\begin{array}{ll} \begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH_2 + H_2 & \qquad 60\% \\ CH_3.CH{=}CH_2 + CH_4 & \qquad 40\% \end{array}\right.$$

$$6.\quad \underset{\text{Tetramethylmethane}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\!\begin{matrix}CH_3\\CH_3\end{matrix}} \xrightarrow{430^\circ} \begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH_2 + CH_4 \qquad 100\%$$

(3) **Dehydrogenation of Alkanes.** Though, as already seen, alkanes can be thermally decomposed to give unsaturated hydrocarbons, rupture of the carbon chains occurs to a very great extent at the reaction temperature. Selective dehydrogenation therefore must be carried out in the **presence of suitable catalysts**, which bring about dehydrogenation at temperatures lower than those at which pyrolysis occurs. The dehydrogenation is much more successful with lower alkanes, which are comparatively stable towards heat, than with the higher ones, which possess increasing tendency to chain rupture. Among the selective catalysts for dehydrogenation of alkanes, the

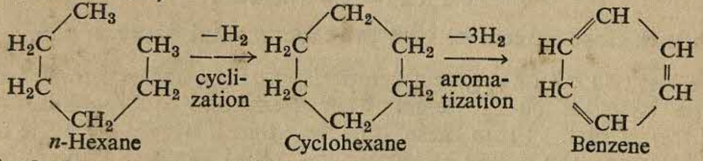
oxides of chromium, molybdenum, vanadium and cerium are the most effective.

The **dehydrogenation of *n*-butane** to butenes is of great commercial interest because of the high importance of butenes and butadiene in both chemical and gasoline manufacture. The process is carried out at 550—590°C, chromic oxide on an alumina support being used as the catalyst. The following reactions are involved :



The process is carried out in two or more steps, and the product, at each step, is separated by fractionation and solvent extraction.

(4) **Aromatization of Alkanes.** A remarkable reaction that alkanes containing six or more carbon atoms undergo is that of conversion into aromatic hydrocarbons under the action of heat and catalysts. Thus, *n*-hexane, when passed over chromic oxide catalyst heated at 460°, yields benzene by ring closure (**cyclization**) and dehydrogenation (**aromatization**) :



Similarly, *n*-heptane yields toluene.

(5) **Heats of Combustion of Alkanes.** On account of the importance of petroleum products as fuels, the facts related with the heats of combustion of paraffin hydrocarbons are of considerable interest to the chemist and the fuel engineer. These can be determined by burning a weighed sample in a *bomb calorimeter*[1], and are tabulated below.

HEATS OF COMBUSTION OF ALKANES IN THE LIQUID STATE

Alkanes	Kilo-cals per mole	Kilo-cals per gram	Kilo-cals per ml.
Methane	211	13·1	5·6
Ethane	368	12·2	6·7
Propane	526	11·9	6·9
n-Butane	685	11·8	6·8
n-Pentane	838	11·6	7·3
n-Hexane	991	11·5	7·6
n-Heptane	1,150	11·5	7·8
n-Octane	1,305	11·4	8·0
n-Decane	1 610	11·3	8·3

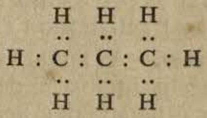
---

[1] For a description of the method, refer to the chapter on Thermochemistry in "Textbook of Physical Chemistry" by Niranjan Singh and Jagindar Singh (Atma Ram & Sons, Delhi).

The figures given in the second column are the heats of combustion in kilo-cals per gram-molecule, as determined experimentally. It is possible to calculate the heats of combustion of organic substances by making use of the observation made by Kharasch that the *heat of combustion of an organic substance is due to the interdisplacement of electrons between the carbon and oxygen atoms.* The quantity of energy involved in this interchange is 26·2 kilo-cals per electron per mole of an alkane. The heat of combustion, H, of per mole is given by the relation

$$H = 26{\cdot}2 \times n$$

where n is the number of valency electrons. Thus in the case of propane



$$\begin{array}{ccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ \mathrm{H} : & \mathrm{C} & : & \mathrm{C} & : & \mathrm{C} & : \mathrm{H} \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

the number of valency electrons is 20. Hence the heat of combustion of propane is

$$= 26{\cdot}2 \times 20 = 524 \text{ kilo-cals},$$

which is in close agreement with the experimental figure of 526.

The last two columns give a comparison of the heats of combustion on the basis of equal weights (per gram) and equal volumes (per millilitre) of fuel. From these, it is clear that if weight were the only consideration, the lower hydrocarbons would be more efficient fuels than the higher ones. However, the volume capacity of a fuel tank or of an incendiary bomb is the more important limiting factor than the weight, and the higher hydrocarbons have an advantage over the lower ones from this point of view, as will be seen from the last column. Ignition characteristics of a fuel have also to be considered, and a balance must be struck between these and the fuel load when making a decision about the fuel to be used for a particular purpose.

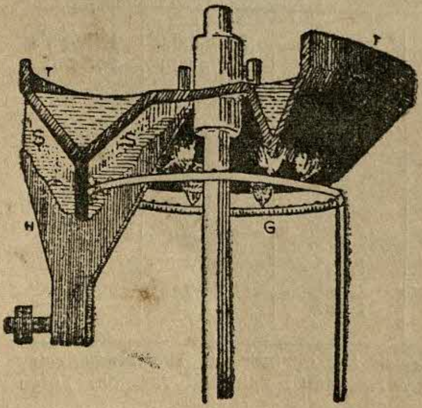


Fig. 1. Apparatus for making Lamp-black. A water-cooled revolving-trough of cast iron (T) is mounted on a hollow shaft. The circular gas burner, G, is fixed up under the trough, and the thick black smoke from the large number of flames deposits on the under-side of the revolving trough. The scraper, S, continuously removes the lamp-black, which falls through the hopper, H, into sacks.

(6) **Incomplete Combustion.—Manufacture of carbon blacks.** The incomplete combustion of hydrocarbons, *i.e*, burning them in an *insufficient* supply of air, is of industrial importance, as it is the basis of the manufacture of carbon blacks. These are used in the manufacture of Indian ink, printer's ink and black paints and as a filler in rubber compounding. An apparatus for the manufacture of carbon blacks from natural gas is shown in Fig. 1.

(7) **Controlled Air Oxidation.** Oxidation of natural gas and low boiling petroleum fractions by means of air, under high pressures, in the presence of finely-divided metals yields methyl alcohol, formaldehyde and formic acid. High boiling mineral oils and waxes from petroleum yield mixtures of higher fatty acids suitable for use in the manufacture of soap.

(8) **Vapour-Phase Nitration.** Until recently, direct nitration of alkanes was of little importance, as the process is troublesome to carry out and gives only low yields. In 1936, Hass was successful in carrying out the nitration in the *vapour phase* with very good results. A gaseous mixture of a hydrocarbon (2 mols) and nitric acid vapour (1 mol) is passed through a narrow tube heated at 400° to 800°. Methane gives a 13 per cent yield of nitromethane at 475°,

$$CH_4 + HNO_3 \rightarrow CH_3NO_2 + H_2O$$

The unreacted methane is recycled through the reaction tube again and again. Ethane and higher homologues give *mixtures* containing, in addition to the expected product, nitroparaffins having fewer carbon atoms than the original alkane. Thus, with propane at 420°, we get :

$$\left.\begin{array}{ll} CH_3.CH_2.CH_2NO_2 & \text{(32 parts)} \\ CH_3.CH(NO_2).CH_3 & \text{(33 parts)} \\ CH_3.CH_2NO_2 & \text{(26 parts)} \\ CH_3NO_2 & \text{(9 parts)} \end{array}\right\} \text{Total yield} = 20\%$$

Nitroparaffins, obtained by the vapour phase nitration process are used as solvents, primary fuels and as starting materials for synthesizing other organic chemicals.

(9) **Alkylation.** This is a condensation reaction taking place between an alkane and an alkene to give a branched-chain alkane. It is of great technical importance, as it is employed in the manufacture of '*Alkylate*', an important 100-octane aviation gasoline (see chapter on Petroleum, sec. 23).

9. Uses of Alkanes.—The chief uses of alkanes are :—

(1) **As fuel.** The complete combustion of alkane mixtures (in the form of natural gas, gasoline, kerosene oil and heavy oil), being a highly exothermic reaction, is of the greatest importance. It provides more than half of world's requirement of industrial energy.

(2) **As source of carbon blacks.** Incomplete combustion of alkanes, particularly in the form of natural gas, gives a fine, fluffy form of

carbon, called **carbon black.** This is used in motor tyres to improve their wearing qualities and strength. It is also used in making shoe and stove polishes, black paints, typewriter carbons, printer's ink and gramophone records.

(3) **Production of alcohols, aldehydes and acids.** Controlled oxidation of lower alkanes is nowadays used in the production of alcohols, aldehydes and carboxylic acids.

(4) **Production of gasoline and olefins.** Cracking of higher alkanes results in the production of lower alkanes and olefins. The former go to form gasoline, while the latter are employed as the raw materials in the production of many organic compounds (see under Petrochemicals, chap. 11).

(5) **Production of hydrogen.** Alkanes, in the form of natural gas, provide a cheap source of industrial hydrogen. This is based on the pyrolysis of methane :

$$CH_4 \xrightarrow{1,000^\circ} C + 2H_2$$

The hydrogen thus obtained finds extensive use in the synthesis of **ammonia**, the hydrogenation of vegetable oils to form **solid and semi-solid fats** and of coal to produce **synthetic petrol.**

Another reaction that is utilized for the production of hydrogen from methane is with steam (see under Methane).

(6) **Production of chloro derivatives.** Chlorination of lower alkanes (from methane upto pentane) is carried out on a commercial scale to give valuable chloro-derivatives that find wide utilization as **solvents** and in the preparation of other organic compounds.

10. Methane, *Marsh Gas*, CH_4.—

Occurrence. Methane is produced in considerable quantities when cellulose and other organic matter undergoes putrefaction under stagnant water. On this account, the gas is found in marshy places; hence the name *marsh gas*. The **natural gas** that issues from the earth in petroleum districts consists of methane and its homologues. Methane also issues from seams in coal-mines, where, by diffusing into the air, it forms an explosive mixture ; hence the name *fire-damp*, given to it by coal-miners. Methane is an important constituent of *coal gas*, in which it is present to the extent of 30 to 40 per cent.

Preparation. (1) Methane is most conveniently prepared in the laboratory by heating fused sodium acetate with dry soda-lime. The active constituent of soda-lime in this reaction is sodium hydroxide. Pure alkali is not employed, because of its being deliquescent and easily fusible.

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

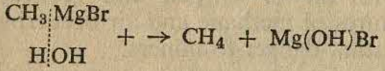
Expt. 1. Heat an intimate mixture of *fused* sodium acetate (1 part) and powdered soda-lime (4 parts) in a copper tube provided with a delivery tube. Collect the issuing gas over water.

(2) Pure methane is most readily obtained by the reduction of methyl iodide with nascent hydrogen (usually from zinc-copper couple and alcohol) :

$$CH_3I + 2H \rightarrow CH_4 + HI$$

For a description of the method see Expt. 3, described under Ethane.

(3) Another method of preparing pure methane is by the decomposition of methylmagnesium bromide with water



$$\begin{array}{l} CH_3\vdots MgBr \\ \quad\vdots \\ \;H\vdots OH \end{array} + \rightarrow CH_4 + Mg(OH)Br$$

(4) Methane may be obtained in the laboratory from aluminium carbide, Al_4C_3, which, when boiled with water, yields the gas contaminated with hydrogen (20 per cent) and other impurities.

$$Al_4C_3 + 12HOH \rightarrow 4Al(OH)_3 + 3CH_4$$

Synthesis.[1] Methane has been synthesized by the following reactions :—

(1) When a current of hydrogen is passed over carbon heated at 1,200°, the elements combine together to yield a small proportion (1 per cent) of methane :

$$C + 2H_2 \rightleftharpoons CH_4$$

The reaction is reversible, since when pure methane is heated at 1,200°, about 99 per cent of it is decomposed into its elements. If carbon be intimately mixed with finely-divided nickel, its combination with hydrogen occurs at lower temperatures and much larger amounts of methane are formed.

(2) **Sabatier** and **Senderens** obtained (1897) an almost quantitative yield of methane by passing a mixture of hydrogen and carbon monoxide or dioxide over finely-divided nickel at 250° to 300° :

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The process has commercial possibilities in localities where natural gas is not available.

(3) The earliest synthesis of methane was carried out by **Berthelot** by passing a mixture of carbon disulphide vapour and hydrogen sulphide over heated copper :

$$CS_2 + 2H_2S + 8Cu \rightarrow CH_4 + 4Cu_2S$$

Physical Properties.—Methane is a colourless and almost odourless gas. It can be liquified at 12° under a pressure of 180 atmospheres.

---

[1] The "**complete synthesis**" of a compound means its formation from the component elements, or from simpler compounds already obtained from elements.

It is very slightly soluble in water, 100 ml. of water at 4° dissolving 5 ml. of the gas.

Chemical Properties.—Methane is neutral in character, and is not affected by acids or alkalis. Nor is it affected by oxidizing agents such as potassium permanganate or dichromate. The more important reactions of methane are :

(2) *Combustibility.* Methane burns in air with practically a non-luminous flame, forming carbon dioxide and water.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

When mixed with air or oxygen and ignited, the gas explodes violently. Mixtures of methane and air occurring in coal mines are therefore of constant danger to miners.

(2) *Action of Chlorine and Bromine.* See sec. 8, reaction (1).

(3) *Vapour-Phase Nitration.* See sec. 8, reaction 8.

(4) *Reactions with Ozone.* When methane is treated with ozonized oxygen, two of its hydrogen atoms are exchanged for an oxygen atom with the production of **formaldehyde.**

$$CH_4 + 2O_3 \longrightarrow HC\overset{H}{\underset{O}{\lessgtr}} + H_2O + 2O_2$$

Formaldehyde

This reaction constitutes a **delicate test for methane**, since even small quantities of formaldehyde may be readily identified by its characteristic reactions and odour.

(5) *Reaction with Steam.* See the section on Natural Gas, chapter 11.

Expt. 2. (*a*) Burn a cylinder full of methane. Notice that the flame is non-luminous. Test the gas left in the cylinder with lime-water ; the latter turns milky.

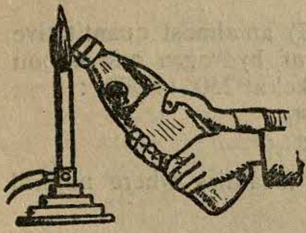
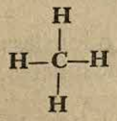


Fig. 2.

(*b*) Pass methane through (*i*) bromine water, (*ii*) sodium hydroxide solution rendered pink with phenolphthalein, (*iii*) dilute sulphuric acid, rendered pink with methyl orange, and (*iv*) potassium permanganate solution, acidified with sulphuric acid. Notice that there is no reaction with any of these reagents.

(*c*) Fill a strong "soda water" bottle one-third with methane and two-thirds with oxygen, and then bring its mouth near the flame (Fig. 2). A powerful and very loud explosion will occur.

Composition of Methane.—Methane being a gaseous hydrocarbon, its composition can be determined by the method explained under sec. 8 (chap. 4).



Constitution of Methane.—Since carbon is tetravalent and hydrogen monovalent, the methane molecule must be represented by the constitutional formula shown in the margin.

11. Ethane. C_2H_6.—This hydrocarbon occurs along with methane in the *natural gas*, and is also found dissolved in petroleum.

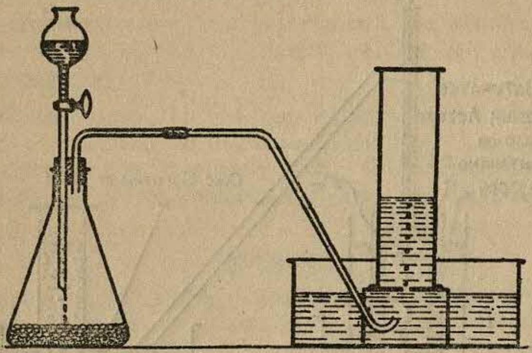


Fig. 3. Preparation of Ethane from Ethyl Iodide.

Preparation. (1) Ethane may be obtained by reactions 1, 2, and 3 used for methane, sodium propionate, C_2H_5COONa, being used in reaction 1, and ethyl iodide and ethylmagnesium bromide in reactions 2 and 3 respectively.

Expt. 3. *Preparatian of Ethane from Ethyl Iodide.* Take 20 grams of granulated zinc in a beaker, and cover it with a 2 per cent solution of cupric sulphate. Allow to stand, until the blue colour is discharged ; then pour off the solution. Repeat the above treatment with cupric sulphate three or four times. Wash the zinc-copper couple, thus obtained, with water and finally with a little alcohol. Then place it in a flask provided with a delivery tube (Fig. 3). Add to the flask 100 ml. of alcohol mixed with a drop or two of dilute sulphuric acid, and then drop ethyl iodide into the mixture from the dropping funnel. Collect the gas over water, and study its properties as in the case of methane.

(2) From *methyl iodide*, by heating with metallic sodium or zinc (**Wurtz reaction**) :—

$$2CH_3I + Zn \longrightarrow CH_3.CH_3 + ZnI_2$$

This reaction may be employed for synthesizing ethane from methane.

(3) *By Anodic Oxidation of Acetate-ion* (**Kolbe's reaction**). When a concentrated aqueous solution of sodium or potassium acetate (or dilute acetic acid) is submitted to electrolysis in a cell divided by a porous partition, the acetate ions lose electrons to the anode (oxidation). The discharged acetate groups, being unstable, undergo decomposition so as to give ethane and carbon dioxide, which are set free at the anode :

$$2CH_3COO^- \longrightarrow CH_3.CH_3 + 2CO_2 + 2e^-$$

At the same time, hydrogen and alkali are set free at the cathode, owing to the reduction of water.

$$2Na^+ + 2H_2O + 2e^- \longrightarrow 2NaOH + H_2$$

The arrangement of the apparatus is shown in Fig. 4. A saturated solution of sodium (or potassium) acetate (containing about 2 per cent of acetic acid) is placed in the porous pot, *P*. The latter is fitted with a cork carrying the T-shaped delivery tube into which

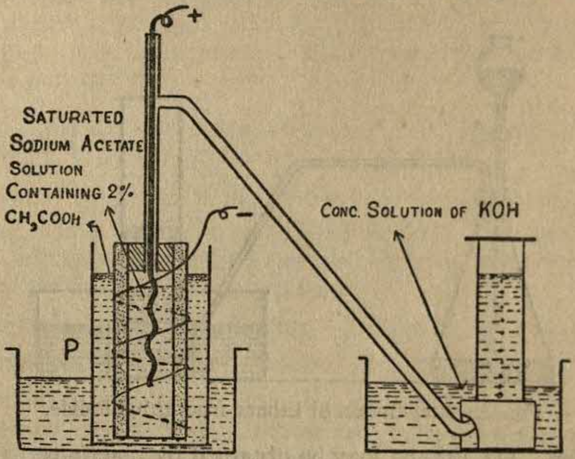


Fig. 4. Electrolytic Preparation of Ethane.

is fused a stout platinum wire to act as the anode. A nickel wire, wound round the cell, serves as the cathode. The porous pot is placed in a beaker containing the same solution as the porous pot itself. The whole apparatus is placed in a trough of cold water, so as to keep the temperature of the electrolyte below 20°. The gas set free at the anode is collected over a strong solution of potassium hydroxide, which absorbs the carbon dioxide.

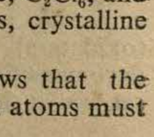
(4) Ethane has been prepared on a large scale by the combination of ethylene and hydrogen in the presence of finely divided nickel :

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

Properties of Ethane.—Ethane, like methane, is a colourless, tasteless gas. Its critical temperature is +34° and critical pressure 50 atmospheres. It is practically insoluble in water and slightly soluble in alcohol.

In chemical properties, ethane closely resembles methane. It readily reacts with chlorine and bromine yielding *substitution products*, all the six hydrogen atoms being successively replaced by chlorine or bromine atoms. The *final* products are hexachloroethane, C_2Cl_6, and hexabromoethane, C_2Br_6, both of which are colourless, crystalline solids.

Constitution of Ethane.—Explosion with oxygen shows that the molecular formula of ethane is C_2H_6. The two carbon atoms must be united directly as a monovalent hydrogen atom could not possibly link them together. Moreover, since the carbon is tetravalent, the two carbon atoms must carry three atoms of hydrogen each. Hence, the structural formula of ethane is as shown in the margin. This view is confirmed by the formation of ethane from methyl iodide by Wurtz reaction.



$$\begin{array}{c}\mathrm{H}\quad\mathrm{H}\\ |\quad\; |\\ \mathrm{H{-}C{-}C{-}H}\\ |\quad\; |\\ \mathrm{H}\quad\mathrm{H}\end{array}$$

12. Higher Members.—**Propane**, $CH_3.CH_2.CH_3$, is also a constituent of natural gas. It can be prepared by the same methods as ethane, and closely resembles the latter in properties.

There exist two **butanes** three **pentanes** and five **hexanes** (sec. 3). All of them, as also the higher members, exhibit the general chemical behaviour described in sec. 8.

13. Petrochemicals Derived from Alkanes.—A very large number of organic substances are now manufactured from alkanes as basic raw materials derived from petroleum. These are known as "*petroleum chemicals*" or '*petrochemicals*' and are described in a later chapter.

QUESTIONS

1. Describe the general methods of preparation and general reactions of the hydrocarbons of the paraffin series. Name six compounds of this series and give their structural formulae.

2. Give an account of the occurrence of methane. How will you prepare a sample of this hydrocarbon in the laboratory and what experiments will you perform to illustrate its important properties? "Methane is a saturated hydrocarbon." Explain this statement.

3. How do the physical properties of the members of the methane series of hydrocarbons vary with increase of the number of carbon atoms in the molecule? What are the characteristic differences in the properties of the saturated and the unsaturated hydrocarbons? (*Andhra, B.Sc., 1952*)

4. How can the following functional groups be introduced into the molecule of an aliphatic hydrocarbon? :—(*a*) Bromo, (*b*) Cyano, (*c*) Aldehyde, (*d*) Amino and (*e*) Amido. (*Bihar, B.Sc., 1955*)

5. Describe various methods by which methane has been synthesised. Describe a method by which you could prepare the gas in the laboratory. How will you distinguish between methane and another hydrocarbon of this series?

6. Write a note on the nomenclature of isomeric paraffins. Write the structural formulae of the following hydrocarbons: *Neopentane, dimethylethylmethane, 1-methyl-5-isopropyl-hexane.*

7. Write the structural formulae for—

(*i*) Dimethylisopropylmethane

(*ii*) 3,4-Dimethyl-4 isopropyloctane (*Punjab, B.Sc., 1960*)

8. Write all the possible structural formulae for a hydrocarbon with the molecular formula C_4H_{8+2}. If you are given a sample of such a hydrocarbon, what methods would you employ to assign to it the appropriate structural formula? (*Rajasthan, B.Sc., 1961*)

9. Outline the methods available for the preparation of saturated hydrocarbons and review their properties. (*Mysore, B.Sc., 1958*)

CHAPTER TEN

UNSATURATED HYDROCARBONS

1. Unsaturated Hydrocarbons.—An *unsaturated* hydrocarbon is one in which the maximum combining capacity of one or more pairs of carbon atoms is not fully utilized. There are two chief homologous series of unsaturated aliphatic hydrocarbons, one represented by *ethylene*, C_2H_4, and the other by *acetylene*, C_2H_2. The former class are called **alkenes**, or **olefins**, and the latter **alkynes** or **acetylene hydrocarbons**.

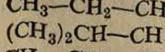
OLEFINS OR ALKENES

2. Nomenclature of Alkenes.—This series of hydrocarbons, of which the first member is ethene or ethylene, C_2H_4, has the **general molecular formula** C_nH_{2n}, and each member has one double bond in the molecule. Two systems of naming olefins are in use.

(1) **Common Names.** The common system of nomenclature for lower members consists in naming the alkene after the alkane having the same number of carbon atoms by replacing the suffix *-ane* by the suffix **-ylene**. In this way, we get the name *ethylene*, *propylene*, *butylene*, etc. This method, however, is inadequate for naming higher members owing to the fact that there are more isomers than there are names. Thus there exist three alkenes having four carbon atoms in the molecule, yet only two names, butylene and isobutylene, are available. This difficulty is met by regarding the higher homologues as *derivatives of the first member* of the series, namely ethylene. In a dialkyl-ethylene, if the two alkyl groups are linked to different carbon atoms of the ethylene chain, it is termed *symmetrical*; if they are linked to the same carbon atom, it is termed *unsymmetrical*. Thus, the names of the **three butylenes** are :—

1.	$CH_3—CH_2—CH=CH_2$	Ethylethylene
2.	$CH_3—CH=CH—CH_3$	Symmetrical dimethylethylene
3.	$(CH_3)_2C=CH_2$	Unsymmetrical dimethylethylene

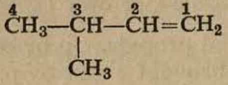
Similarly, the common names of the **five pentylenes** are :

1.	$CH_3—CH_2—CH_2—CH=CH_2$	*n*-Propylethylene
2.	$(CH_3)_2CH—CH=CH_2$	Isopropylethylene
3.	$CH_3—CH_2—CH=CH—CH_3$	*sym*-Methylethylethylene
4.	 $\begin{matrix}CH_3\\C_2H_5\end{matrix}>C=CH_2$	*unsym*-Methylethylethylene
5.	$(CH_3)_2C=CH—CH_3$	Trimethylethylene

(2) **IUC System.** The IUC system of naming alkenes is identical

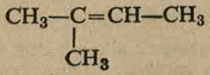
with that described in the case of alkanes, the suffix *-ane* being replaced by **ene**. The position of side-chains and of the double bond is located by means of numerals. The numeral used for locating the double bond refers to the number of carbon atom on which the double bond *starts*. In case the double bond is between a carbon atom of the main chain and that of the side chain, the olefin is named as a derivative of the **longest chain containing the double bond**. The following examples illustrate the method of nomenclature :—

1. $\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$ Pentene-1

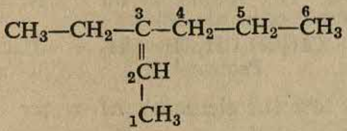
2. 

$\overset{4}{C}H_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{2}{C}H=\overset{1}{C}H_2$ 3-Methylbutene-1

3. $CH_3-CH_2-CH=CH-CH_3$ Pentene-2

4. 

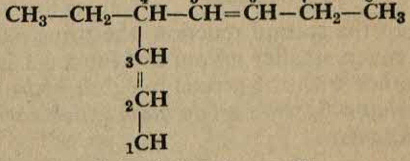
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$ 2-Methylbutene-2

5. 

$CH_3-CH_2-\underset{\displaystyle {}_1CH_3}{\underset{|}{\underset{{}_2CH}{\underset{\|}{\overset{3}{C}}}}}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$ 3-Ethylhexene-2

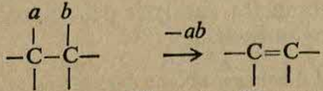
In the older literature, the position of the double bond is indicated by the Greek letter △ followed by the number of the carbon atom where the double bond starts. Thus, the structure 5 above is named 3-ethyl-△-2-hexene.

In the case of **dialkenes** and **trialkenes**, *i.e.*, hydrocarbons containing respectively two and three double bonds in the molecule, the position of each of the double bonds in the chain is indicated by numerals and the suffix **diene** or **triene** is used in the name. Thus the diene of the structure shown in the margin is named 4-ethyl-2,5-octadiene.



$CH_3-CH_2-\underset{\displaystyle {}_1CH}{\underset{|}{\underset{{}_2CH}{\underset{\|}{\underset{{}_3CH}{\underset{|}{\overset{4}{C}H}}}}}}-\overset{5}{C}H=\overset{6}{C}H-\overset{7}{C}H_2-\overset{8}{C}H_3$

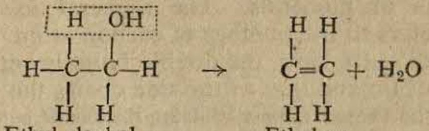
3. Methods of Formation of Alkenes.—The principle on which the **formation of an alkenic double bond** is based is the *removal of atoms or groups from two carbon atoms already joined by a single bond* :—



$$\begin{array}{c} a\quad b\\ |\quad\ | \\ -C-C- \\ |\quad\ | \end{array} \xrightarrow{-ab} \begin{array}{c} -C=C- \\ |\quad\ | \end{array}$$

a and *b* may be similar or different. The reagents and conditions required to bring about this elimination, of course, depend upon the nature of the atoms or groups to be removed.

(1) **Dehydration of alcohols.** The usual method of preparing lower alkenes in the laboratory is by dehydration of alcohols, *e.g.*,



$$\text{H}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{H} \rightarrow \underset{\text{H}}{\overset{\text{H}}{\text{C}}}=\underset{\text{H}}{\overset{\text{H}}{\text{C}}} + H_2O$$

Ethyl alcohol Ethylene

Hot, concentrated sulphuric acid, phosphoric acid or zinc chloride are the usual dehydrating agents employed for this purpose. In the reaction between ethyl alcohol and sulphuric acid, ethyl hydrogen sulphate is produced as the intermediate product (see Sec. 7).

The best method for preparing ethylene and propylene is by **catalytic dehydration** of ethanol and propanol. This is brought about by passing the alcohol vapour over a suitable **dehydration catalyst**, such as alumina or thoria heated at 350° to 400°. Under these conditions, the alcohol is decomposed quantitatively into alkene and water.

Catalytic dehydration of higher alcohols gives a mixture of alkenes due to the shifting of the double bond under the influence of the catalyst. Thus, butanol-1 gives a mixture of butene-1 and butene-2. This shifting of the double bond is prevented by using the acetates (or stearates) of the alcohols ; *e.g.*,

$$\underset{\text{Pentanol-1 acetate}}{CH_3CH_2CH_2CH_2CH_2OOCCH_3} \rightarrow \underset{\text{Pentene-1}}{CH_3CH_2CH_2CH{=}CH_2} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Secondary and tertiary alcohols lose the elements of water more readily than primary alcohols.

(2) **Removal of elements of hydrogen halide (HCl, HBr or HI) from alkyl halides.** This is brought about by heating the halide with a solution of potassium hydroxide in ethyl alcohol ("*alcoholic potash*") ; *e.g.*,

$$\underset{\text{Bromoethane}}{CH_3.CH_2Br} + KOH \rightarrow \underset{\text{Ethene}}{H_2C{=}CH_2} + KBr + H_2O$$

$$\underset{\text{2-Bromobutane}}{CH_3.CH_2.CHBr.CH_3} + KOH \rightarrow \underset{\text{2-Butene}}{CH_3.CH{=}CH.CH_3} + KBr + H_2O$$

In the second reaction, the principal product is butene-2, though a much smaller amount of butene-1 is also formed. This is in accordance with the **general rule** that *hydrogen is more readily removed from that adjacent carbon atom which carries a smaller number of hydrogen atoms.*

It should be noted that the treatment of alkyl halides with alcoholic potash results in the production of alcohols and ethers in addition to alkenes (see under reactions of alkyl halides, chap. 12, sec. 4).

Sabatier and Mailhe have shown that finely-divided nickel, copper or cobalt can bring about the catalytic decomposition of alkyl halides into olefines and halogen hydrides.

(3) **Dehalogenation of dihalogen alkane derivatives.** An alkene may be prepared from a dihalogen derivative having the two halogen atoms attached to *adjacent* carbon atoms by dehalogenation with zinc-copper couple or sodium, etc. Thus, pure ethene is conveniently

prepared by treatment of 1-2-dibromoethane, dissolved in aqueous alcohol with zinc-copper couple :—

$$\underset{\text{1, 2-Dibromoethane}}{CH_2Br.CH_2Br} + Zn \rightarrow \underset{\text{Ethene}}{H_2C{=}CH_2} + ZnBr_2$$

The method, however, is of limited application on account of non-availability of dihalogen derivatives except when they have been prepared *from* the corresponding alkenes.

(4) **Decarboxylation of anions of saturated dicarboxylic acids.** When concentrated solutions of potassium salts of saturated dicarboxylic acids having the two carboxyls in *adjacent* positions on the carbon chain (*e.g.*, succinic acid) are submitted to electrolysis, we get olefins. The reaction consists in the **oxidation of the anion** of the salt at the anode,

$$\underset{\text{Succinate ion}}{\begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array}} \xrightarrow[-2e^-]{\text{anodic oxidation}} \underset{\text{Ethene}}{\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}} + 2CO_2$$

so that a mixture of alkene and carbon dioxide is evolved at the anode[1].

(5) **Grignard Synthesis of 1-Alkenes.** An excellent method of synthesis of *pure* alkenes with a *terminal double bond* consists in adding allyl bromide to an ethereal solution of the Grignard reagent obtained from an alkyl halide, when a coupling of the two hydrocarbon residues occurs. Thus, with methylmagnesium bromide we get 1-butene :

$$\underset{\text{Allyl bromide}}{CH_2{=}CHCH_2}\boxed{Br + BrMg}CH_3 \rightarrow \underset{\text{1-Butene}}{CH_2{=}CHCH_2CH_3} + MgBr_2$$

(6) **Pyrolysis of Wood, Coal and Petroleum.** Olefins are produced, together with paraffins, by the destructive distillation of many carbonaceous materials, such as wood, lignite and coal. They are also formed by the "cracking" of higher paraffins (page 142).

3. **Physical Properties of Alkenes.**—As in the case of the alkane series, alkenes show a gradual change in their physical properties. The lower members, up to C_4H_8, are gases, the following fourteen or so are liquids, while the higher ones are solids. The boiling-points of the corresponding hydrocarbons of the methane and the ethylene series lie very close together, but the melting-points of the alkenes are somewhat lower than those of the alkanes. Alkenes are readily soluble in alcohol, but practically insoluble in water.

Butene-2 and other *symmetrical* dialkylethylenes exhibit **cis-trans isomerism** (p. 119).

The more important physical constants of a few alkenes are given in the Table on next page.

4. **Chemical Reactions of Alkenes.**—The most characteristic property of alkenes is their power of addition, though under special

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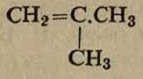
[1] At the cathode, *reduction* of water occurs, and hydrogen and alkali are produced :

$$2K^+ + 2H_2O \xrightarrow{+2e^-} 2KOH + H_2$$

conditions they can also undergo substitution reactions. They directly add on a variety of substances, such as hydrogen, halogens, halogen hydracids, etc., yielding saturated compounds, the double bond of the alkene passing into a single bond. Other types of reactions suffered by alkenes include isomerization, alkylation and polymerization.

Name	Formula	M.P., °C	B.P., °C	Sp. Gr. (as liquid)
Ethene	$CH_2=CH_2$	−169·15°	−103·71°	0·5676 at −102°C
Propene	$CH_2=CHCH_3$	−185·25	− 47·70	0·6104 at −47·7
Butene-1	$CH_2=CHCH_2CH_3$	−185·35	− 6·26	0·6255 at − 6·47
Butene-2	$CH_3CH=CHCH_3$			
cis-		−138·91	+ 3·72	0·6448 at 0°
trans-		−105·55	+ 0·88	0·6269 at 0°
2-Methyl-propene-1	 $CH_2=C(CH_3).CH_3$	−140·35	− 6·90	0·6266 at −6·6°

(1) **Addition of Hydrogen—"Hydrogenation."** Combination of alkenes with hydrogen gas to produce an alkane is a *reversible* and *exothermic* reaction, *e.g.*,

$$CH_2=CH_2 + H_2 \rightleftharpoons CH_3.CH_3 + 32{\cdot}5 \text{ kcals.}$$

Below 100°, equilibrium lies almost wholly on the side of the alkane. At higher temperatures (350° to 450°), an alkane decomposes to give the corresponding alkene and hydrogen. Both the forward and the backward reaction requires the use of catalysts. Finely-divided platinum or palladium at ordinary temperatures and finely-divided nickel at about 150° are the best known hydrogenation catalysts, while amorphous chromic oxide, Cr_2O_3, is a very good dehydrogenation catalyst.

Catalytic hydrogenation of Alkenes provides an important method for **preparation of pure alkanes.** On the other hand, the most important commercial process for the production of ethylene utilizes the cracking of propane from petroleum refinery gases or from natural gas.

(2) **Addition of Halogens.** Alkenes very easily combine with chlorine and bromine at the ordinary temperatures ; *e.g.*,

$$\underset{\text{Ethylene}}{CH_2=CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

The alkene may be shaken with bromine water or treated with liquid bromine with effective cooling. In certain cases, a solution of the halogen in carbon tetrachloride or carbon disulphide may be used with advantage.

With iodine, the addition is very slow, except in the presence of strong light, and the reaction is reversible ; *e.g.*,

$$CH_2=CH_2 + I_2 \overset{\text{light}}{\rightleftharpoons} CH_2I.CH_2I$$

It is interesting to note that at high temperatures, chlorine and bromine react with alkenes by **substitution** ; *e.g.*,

$$\underset{\text{Propene}}{H_2C{=}CH.CH_3} + Cl_2 \xrightarrow{\text{at } 500^\circ C} \underset{\text{Allyl chloride}}{H_2C{=}CH.CH_2Cl} + HCl$$

(3) **Addition of Halogen Hydracids.** Alkenes combine with HCl, HBr and HI, giving alkyl halides ; *e.g.*,

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + HI \rightleftharpoons \underset{\text{Ethyl iodide}}{CH_3.CH_2I}$$

The reaction occurs most readily with hydrogen iodide. Hydrogen chloride and hydrogen bromide, on the other hand, react extremely slowly. In the presence of certain catalysts, however, the combination occurs quite readily. Thus, when ethylene and hydrogen chloride are passed over bismuth chloride heated at 100°, we get ethyl chloride,

$$CH_2{=}CH_2 + HCl \rightleftharpoons CH_3.CH_2Cl$$

The reaction is reversible, and at 500° ethyl chloride gets decomposed completely into ethene and hydrogen chloride.

The addition of halogen hydracids to propene and higher alkenes occurs in such a way that *the hydrogen atom gets attached to that carbon atom of the double bond which already holds the larger number of hydrogen atoms* (**Markownikoff's rule**). For example,

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + HBr \rightleftharpoons \underset{\text{2-Bromopropane}}{CH_3.CHBr.CH_3}$$

Peroxide Effect. It is interesting to note that the addition of HBr (but *not* HCl) to alkenes containing terminal carbon-carbon double bond can be *reversed* by the presence of organic peroxides. Thus, when a mixture of liquid propene and liquid hydrogen bromide is kept in a sealed tube at ordinary temperature with exclusion of oxygen, we get 2-bromopropane exclusively in accordance with the Markownikoff rule. If, however, a small quantity of benzoyl peroxide be added to the mixture, the product consists of 1-bromopropane (80 per cent) and 2-bromopropane (20 per cent). This phenomenon, discovered by M.S. Kharasch, is known as the *peroxide effect*.

(4) **Addition of Sulphuric Acid.** Alkenes are dissolved by concentrated sulphuric acid, forming alkylsulphuric acids. Ethene is absorbed by concentrated sulphuric acid at about 80° to give ethylsulphuric acid :

$$CH_2{=}CH_2 + H_2SO_4 \rightleftharpoons CH_3.CH_2.HSO_4$$

On heating to higher temperatures, the reaction is reversed and ethene is evolved. With higher alkenes, the addition occurs in accordance with the *Markownikoff rule*, *e.g* ,

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2SO_4 \rightleftharpoons \underset{\text{Isopropylsulphuric acid}}{(CH_3)_2CH.HSO_4}$$

On diluting the reaction product with water, the alkylsulphuric acid is hydrolysed with the production of the corresponding alcohol ; *e.g.*,

$$CH_3.CH_2.HSO_4 + HOH \rightleftharpoons \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + H_2SO_4$$

On distilling the diluted liquid, the alcohol passes over. This reaction is utilized in the commercial preparation of alcohols, *e.g* , ethyl alcohol from ethylene, isopropyl alcohol from propylene and trimethylcarbinol from isobutylene. These and other alkenes are obtained in large quantities from coke-oven gas and from gas produced by "cracking" of mineral oils.

(5) **Addition of Water.** Direct hydration of alkenes in the presence of certain catalysts is possible. Thus, ethylene and water combine together at low temperatures and high pressures in the presence of suitable catalysts (*e.g.*, aluminium oxide, manganous acid phosphate or barium acid phosphate) :—

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O \rightleftharpoons \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

Within the last few years, this process has found special favour for the commercial preparation of ethyl alcohol from ethylene.

The hydration of higher alkenes proceeds in accordance with *Markownikoff's rule ; e.g.*,

$$\underset{\text{Propylene}}{CH_3.CH{=}CH_2} + H_2O \rightleftharpoons \underset{\text{Isopropyl alcohol}}{CH_3.CH(OH).CH_3}$$

(6) **Addition of Hypohalogen Acids.** When an alkene is treated with an aqueous solution of chlorine or bromine, then, besides the addition of the halogen to the alkene (reaction 2), another reaction also occurs, namely the addition of hypochlorous acids or hypobromous acid (which are always present in the aqueous solutions of chlorine and bromine respectively) :—

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

$$CH_2{=}CH_2 + HOCl \longrightarrow \underset{\text{Ethylene chlorohydrin}}{CH_2Cl.CH_2OH}$$

In the addition of hypohalogen acids to higher alkenes, it is the *halogen* atom that goes to the double-bond carbon atom carrying the larger number of hydrogen atoms ; *e.g.*,

$$CH_3.CH{=}CH_2 + HOCl \rightarrow \underset{\text{1-chloropropanol-2}}{CH_3.CH(OH).CH_2Cl}$$

(7) **Hydroxylation.** Alkenes are readily hydroxylated, *i.e.*, add on hydroxyl groups, to form glycols ; *e.g.*,

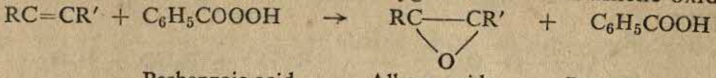
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O + O \rightarrow \underset{\text{Ethylene glycol}}{CH_2(OH).CH_2(OH)}$$

The hydroxylation of an alkene may be carried out by means of—

(*i*) A cold, dilute, alkaline solution of *potassium permanganate.* In acid solution, the oxidation occurs so rapidly that the reaction is employed as a **test for the presence of a double bond** in an organic compound. An excess of the reagent (whether acidic or alkaline) must however be avoided, as the glycols, first produced, are further oxidized with rupture of the carbon chain (*see* below).

(*ii*) *Hydrogen peroxide* in glacial acetic acid (90 per cent solution). This reagent has the advantage of being without any further action on the initial product.

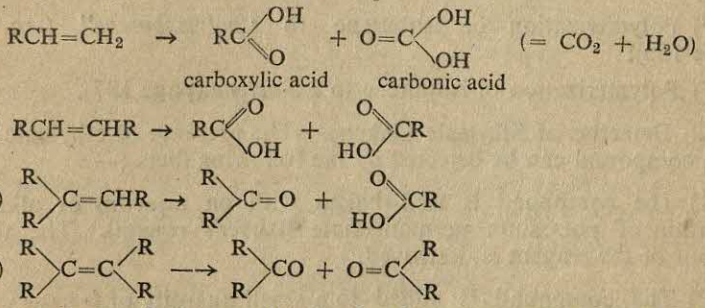
(8) **Formation of Alkene Oxides.** When an alkene is treated with perbenzoic acid, it adds on an atom of oxygen to form an alkene oxide :



Perbenzoic acid Alkene oxide Benzoic acid

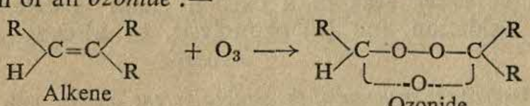
The product, when heated with water under pressure, gets hydrolysed to give a glycol.

(9) **Exhaustive Oxidation.** When an alkene is treated with an excess of acidified permanganate solution, or with chromic acid solution, the intermediate product (*viz.*, the glycol) is destroyed with rupture of the carbon chain at the point of the original double bond and the production of two oxidized fragments (carboxylic acids or ketones). The products obtained depend on the position of the double bond in the alkene molecule and the number of hydrogen atoms on the doubly bound carbon atoms. In each case, the oxidation occurs in such a way that *each of the doubly bound carbon atoms takes up an oxygen atom, while each of the hydrogen atoms carried by the two carbons gets oxidized to the OH group* (exhaustive oxidation). The following are typical illustrative examples :


(*i*) RCH=CH_2 → RC(=O)OH + O=C(OH)OH (= CO_2 + H_2O)
carboxylic acid
carbonic acid
(*ii*) RCH=CHR → RC(=O)OH + HO(O=)CR
(*iii*) R₂C=CHR → R₂C=O + HO(O=)CR
(*iv*) R₂C=CR₂ → R₂CO + O=CR₂

An analysis of the products of exhaustive oxidation therefore reveals the **structure of the alkene.**

(10) **Ozonide Formation and Ozonolysis.** This affords an even more valuable method of **determining the structure of an alkene.** When ozonized oxygen is passed through a solution of an alkene in an inert solvent (*i.e.* a solvent not attacked by ozone, *e.g.*, CCl_4, C_2H_5Br) at low temperature, the ozone molecule adds on to the alkene with the production of an *ozonide* :—



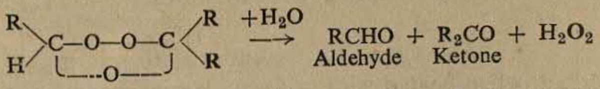
Alkene Ozonide

The ozonide[1], when warmed with water[2], gets decomposed into hydrogen peroxide and an aldehyde or ketone or both depending on the substituents present in the alkene. Thus, in the above case we get :

---

[1] Since ozonides are unstable and explosive, they are *not* isolated but decomposed *in situ.*

[2] As hydrogen peroxide reacts with some aldehydes and ketones, ozonides are not decomposed with water alone, but with water and a reducing agent (*e.g.*, $NaHSO_3$ solution or a suspension of zinc dust in water) which will destroy hydrogen peroxide.



By identifying the aldehydes and ketones formed, the **structure of the alkene** is established. The combined process of the addition of ozone to an alkene followed by the decomposition of the ozonide, described above, is known as **ozonolysis.**

(11) **Alkylation of Alkenes.** Alkenes can be made to combine with alkanes under suitable conditions of temperature, pressure and catalysis. An example of great practical importance is the addition of isobutane to isobutene to produce iso-octane described on page 187.

(12) **Polymerization of Alkenes.** Alkenes show a strong tendency to polymerize. We may here give three important examples :—

(*i*) Conversion of ethene into "*polythene*" (*see* sec. 8, page 164).

(*ii*) Polymerization of isobutene to "*polyisobutene*" (sec. 10, page 165).

(*iii*) Polymerization of isobutene to *iso-octene* (page 187).

5. **Detection of Ethylenic Linkage.**—The presence of ethylenic link in a compound can be detected by the following facts :—

(1) The compound is well-shaken with an aqueous or alkaline solution of potassium permanganate (**Baeyer's reagent**). The violet colour of the reagent is destroyed.

(2) The compound is added to a small quantity of **bromine water,** or bromine dissolved in carbon disulphide, and the mixture shaken. The colour of bromine is discharged.

(3) The compound is mixed with finely divided nickel and warmed, and then pure and **dry hydrogen gas** is passed. The gas is absorbed by the compound. This absorption of hydrogen occurs at room temperature if nickel be replaced by platinum.

The **position of double bond** in a carbon chain is determined by (*i*) exhaustive oxidation and (*ii*) ozonolysis, as already explained above.

Example 1. *Deduce the structure of the three different olefins, which give the following products respectively on ozonolysis :—*

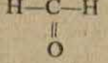
(*i*) *a one-carbon aldehyde and a three-carbon ketone.*

(*ii*) *a two-carbon aldehyde and a four-carbon aldehyde containing an isopropyl group.*

(*iii*) *a three-carbon ketone and a four-carbon ketone.* (*Lucknow, B.Sc., 1962*)

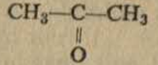
On ozonolysis, the molecule of an alkene gets ruptured at the double bond to produce an aldehyde or ketone, or both, depending on the structure of the hydrocarbon. In the present three cases, we have :—

(*i*) The products being a one-carbon aldehyde and a three-carbon ketone, *viz.*,



$$H{-}\underset{\underset{O}{\|}}{C}{-}H$$

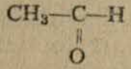
and



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

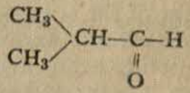
the alkene must have the structure, $H_2C=C(CH_3)_2$, *i.e.*, it is *unsymmetrical dimethylethylene.*

(*ii*) Here, the products are a two-carbon aldehyde and a four-carbon aldehyde containing an isopropyl group, *viz.*,



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}H$$

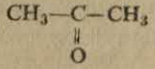
and



$$(CH_3)_2CH{-}\underset{\underset{O}{\|}}{C}{-}H$$

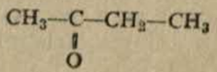
The alkene therefore must have the structure, $CH_3{-}CH{=}CH{-}CH(CH_3)_2$, *i.e.*, it is *symmetrical methylisopropylethylene.*

(*iii*) The products, in this case, are a three-carbon ketone and a four-carbon ketone, *viz.*,

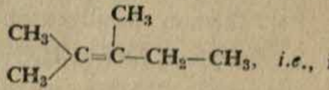


$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

and



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_3$$

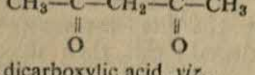
The alkene must have the structure,  $(CH_3)_2C{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_3$, *i.e.*, it is *trimethylethylethylene.*

Example 2. *A hydrocarbon,* C_7H_{10}, *on oxidation, gives the products :*

$$O{=}C(CH_3).CH_2.C(CH_3){=}O \quad \textit{and} \quad HOOC.COOH$$

What is its structure ? (*Lucknow, B.Sc., 1959*)

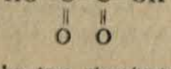
Of the two products of exhaustive oxidation, one is a diketone, *viz.*,



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

(Pentane-2, 4-dione)

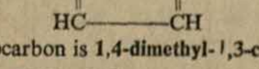
and the other a dicarboxylic acid, *viz.*,



$$HO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH$$

(Ethanedioic acid)

Examination of the two structures reveals that the original hydrocarbon molecule was a cyclic one, consisting of *five* carbon atoms and *two* double bonds. Joining up the two fragments and replacing the two OH groups by hydrogen atoms, we get the structure of the hydrocarbon :



Hence, the given hydrocarbon is **1,4-dimethyl-1,3-cyclopentadiene.**

The molecular formula, C_7H_{10}, fully supports the conclusion.

6. Estimation of Ethylenic Group.—The number of the ethylenic groups in a compound can be determined by the following methods :—

1. The ethylenic compound of the known molecular formula is

treated with hydrogen gas in the presence of finely divided nickel and the new substance thus produced is quantitatively analysed for its molecular composition. If the latter contains two hydrogen atoms more in the molecule, the compound under examination contains one ethylenic link. If four hydrogen atoms have been absorbed, there are two ethylenic links in the compound. In short, the number of ethylenic links is given by hydrogen atoms absorbed divided by two.

2. The most handy method is one of determining the iodine value of the compound. The method consists in mixing a known weight of the compound dissolved in carbon tetrachloride, or chloroform, with a known volume of iodine and iodine monochloride solution in acetic acid. After allowing the mixture to stand overnight, it is titrated against a standard thiosulphate solution. A blank titration with the same volume of the iodine solution is also carried out. The difference between the two titrations gives a measure of the iodine used up by the known weight of the compound. From this weight of iodine we can calculate the weight of iodine required to saturate one gram molecule of the unsaturated compound. Then from the following relation, the number of ethylenic groups can be determined :—

2×127 gram of iodine ≡ one ethylenic group.

7. Ethylene, *Ethene*, $H_2C=CH_2$.

Occurrence. Ethylene occurs to the extent of about 5 per cent in coal gas and in the gas from the coking ovens. It is also present in wood-gas.

Preparation. Ethylene may be obtained by any of the general methods already described (sec. 2). In the laboratory, it is usually obtained by heating a mixture of ethyl alcohol and concentrated sulphuric acid to about 160°C. The reaction has been shown to take place actually in **two stages**. In the first instance, ethyl hydrogen sulphate, $C_2H_5.HSO_4$, is produced ; this then decomposes to give ethylene and water :

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5.HSO_4 + H_2O$$
$$C_2H_5.HSO_4 \rightleftharpoons C_2H_4 + H_2SO_4$$

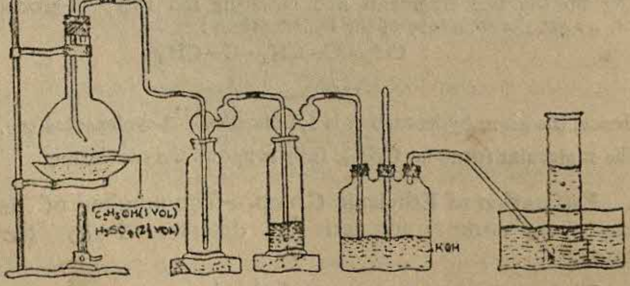


Fig. 1. Preparation of Ethylene.

Expt. 1. A mixture of 30 ml. of alcohol and 75 ml. of concentrated sulphuric acid, together with enough sand to form a thin paste, is placed in a large size, round-bottom flask provided with a delivery tube and a dropping funnel (Fig. 1). The stem of the latter should be drawn out to a fine point and slightly bent, so that it would be kept filled with liquid and thus prevent the escape of the gas through it. The object of adding sand to the flask is to prevent frothing. The flask is heated on a sand bath, until a steady stream of gas is evolved (160-165°C). When the evolution of gas becomes slow, a further supply may be obtained by dropping a mixture of equal volumes of alcohols and concentrated sulphuric acid. The evolved ethylene is contaminated with alcohol and ether vapours, carbon dioxide and sulphur dioxide. It is, therefore, passed first through a well cooled empty wash bottle, in order to condense alcohol and ether vapours, then through one or more wash-bottle containing a solution of potassium hydroxide to remove CO_2 and SO_2. The gas thus purified is collected over water in glass cylinders.

An alternative method of preparing ethylene, free from carbon dioxide and sulphur dioxide, consists in dropping ethyl alcohol into syrupy phosphoric acid heated to about 220°. As the reaction is continuous, an almost unlimited amount of the alcohol can be decomposed by a relatively small amount of phosphoric acid.

Expt. 2. About 50 ml. of syrupy phosphoric acid (sp. gr. 1·75) is placed in a 250 ml. distillation flask provided with a dropping funnel (the stem of which is drawn out to a fine point reaching to the bottom of the flask) and a thermometer (the bulb of which dips in the acid). The flask is heated on a sand bath, until the temperature rises to 220°, and then a quantity of alcohol is run in very slowly. The evolved gas is passed through a wash bottle surrounded by ice, in order to condense water and ether vapours, and is then collected over water.—

Commercial Preparation. Ethylene nowadays is one of the most important starting materials for the production of aliphatic chemicals. It is prepared on a very large scale from the following sources :—

(1) **From natural gas or petroleum refinery gases.** When these gases are passed through heated tubes, containing Cr_2O_3 as the catalyst, the ethane and propane components undergo pyrolysis, yielding ethylene.

(2) **From alcohol.** When ethyl alcohol vapour is passed through heated tubes containing kaolin, it undergoes decomposition yielding ethylene and steam :—

$$C_2H_5OH \rightleftharpoons C_2H_4 + H_2O$$

Physical Properties. Ethylene is a colourless gas having a faint ethereal odour. It is sparingly soluble in water, but fairly so in alcohol and ether.

Chemical Properties. (1) Ethylene burns with a luminous flame, and, like other hydrocarbons, forms an explosive mixture with air or oxygen.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

(2) It shows the various addition reactions described under sec. 4.

(3) Willstatter and Bommer have found that the oxidation of ethylene by atmospheric oxygen yields a fairly good yield of formaldehyde :

$$CH_2{=}CH_2 + O_2 \rightarrow 2H.CHO$$

Expt. 3. (*a*) Ignite a cylinder full of ethylene. Notice that the gas burns with a bright flame.

(*b*) Invert a jar containing ethylene over another containing chlorine. Notice that the colour of chlorine soon disappears, with the simultaneous production of oily drops of ethylene chloride.

(*c*) Repeat the experiment, using bromine vapour instead of chlorine.

(*d*) Pour some bromine water into a jar of ethylene and shake. Notice that the colour of bromine disappears.

(*e*) Repeat the above experiment with a dilute, acidified solution of potassium permanganate.

Constitution. (See chap. 5, sec. 10).

Uses. (1) Considerable quantities (60 million gallons a year) of ethyl alcohol are now made in the U.S.A. from ethylene obtained by "cracking" petroleum or natural gas.

(2) Ethylene is now being used instead of acetylene for *cutting* and *welding*. Though inferior to acetylene, so far as the flame temperature goes, it has a distinct advantage over the latter in that it can be stored and transported in cylinders under high pressures without danger of explosion.

(3) It is also finding an extensive use in the citrus fruit industry. Fruit is gathered and transported before it is fully ripe. On arrival, it is kept for a few days in an atmosphere containing a small proportion of ethylene. The gas makes the fruit develop colour and ripen quickly. If potatoes are treated with ethylene before planting, the dormant period, before growth of the plant begins, is much shortened.

(4) In recent years, ethylene has come into large use as an anaesthetic in place of ether.

(5) Large quantities of ethylene are used in the preparation of *ethylene chlorohydrin*, *ethylene chloride*, *glycol* and, during war days, *mustard gas* and *polythene* (Sec. 8).

8. Polythene.—When liquid ethylene under very high pressure (1,000 to 1,200 atm.) is heated at 200° to 400° with a small proportion of oxygen (catalyst), a very large number (70 to 700) of molecules combine together to form a long chain :

$$-CH_2.CH_2-(CH_2.CH_2)_n-CH_2.CH_2-$$

The product, called *polythene*, is a **"high polymer"** of ethylene, and has an average molecular weight of 2,000 to 20,000 depending on the temperature and pressure employed. This type of addition of molecules to form long chains is called **addition polymerization**, and is undergone by molecules containing unsaturated bonds.

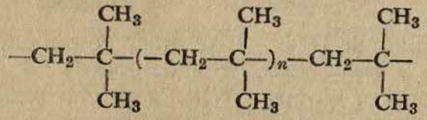
Polythene is a transparent tough solid (m. p. about 118°), and has very valuable properties as an insulator which made it of great importance in radar during the Second World War. It is much used as sheathing for electrical cables, and in making refrigerator dishes, aprons, bags and tablecloths.

9. Higher Homologues of Ethylene.

Propylene (*propene*), $CH_3.CH=CH_2$, is obtained as a by-product in the cracking of heavy oils. It is employed in the manufacture of isopropyl alcohol.

Three **butylenes**, C_4H_8, are theoretically possible. All of these are known, but are of little importance. Of the four isomeric **pentylenes**, C_5H_{10}, one only, *viz.*, **Trimethyl-ethylene**, $(CH_3)_2.C=CH.CH_3$ is important. It is commercially obtained from isoamyl alcohol (*q. v.*) by heating the latter to 200°. It is used, under the name of **pental**, as a narcotic of short duration.

10. Polyisobutylene.—When isobutylene, $CH_2=C(CH_3)_2$, is treated at low temperatures (below $-40°C$) with a suitable catalyst ($AlCl_3$ or BF_3), a high polymer of isobutylene with a molecular weight of 70,000 to 400,000 and having the structure :



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-(-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-)_n-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-$$

is obtained. The lower polymers are viscous liquids, which are used as viscosity stabilizers for lubricating oils, while the higher ones are tough, elastic solids having the properties of unvulcanized rubber. On account of its saturated nature, polyisobutylene is incapable of being vulcanized. It cannot be considered as a synthetic rubber, because it cannot be substituted for rubber in the manufacture of most articles.

DIALKENES

11. General.—The dialkenes contain two double bonds and have the general formula C_nH_{2n-2}. In chemical behaviour the hydrocarbons of this series resemble alkenes, and combine with *four* monovalent atoms or groups. They differ from the alkynes (with which they are isomeric) in forming no copper or silver derivaties. On the other hand, they give precipitates with a solution of mercuric chloride.

12. Butadiene (*1,3-Butadiene*), $CH_2=CH.CH=CH_2$, is the simplest conjugated dialkene. It is prepared on a large scale by a variety of methods, one of which, *viz.*, dehydrogenation of *n*-butane, has already been mentioned (page 145).

Butadiene is a gas (b. p. —2·6°C). It resembles isoprene in chemical behaviour, and, in the presence of sodium as catalyst, polymerizes to a product which was once used as a rubber substitute under the name '*Buna*' (*bu*tadiene+*Na*). This has now been replaced by a copolymer of butadiene and styrene, called '*Buna S*' (see sec. 6). Butadiene is getting increasingly important not only as a polymer component of synthetic rubber but also as an "intermediate" for synthesizing a great variety of organic compounds.

A very characteristic reaction that butadiene and other conjugated dialkenes undergo is the **Diels-Alder Condensation**, described in the chapter on "Alicyclic Compounds" (sec. 3).

13. Isoprene.—$H_2C=C(CH_3).CH=CH_2$, or *2-methyl-1, 3-butadiene*, because of its close relation to caoutchouc and terpenes is the most important of the diolefines. It is produced (together with trimethyl ethylene and dipentene) by the dry distillation of caoutchouc, but the yield is very poor (about 2 per cent). On a commercial scale, isoprene may be obtained from the isoamyl alcohol got from fusel oil in the following three steps :

$$\underset{\text{Isoamyl alcohol}}{(CH_3)_2CH.CH_2.CH_2OH} \xrightarrow{HCl} \underset{\text{Isoamyl chloride}}{(CH_3)_2CH.CH_2.CH_2Cl} \xrightarrow{\text{Chlorination}}$$

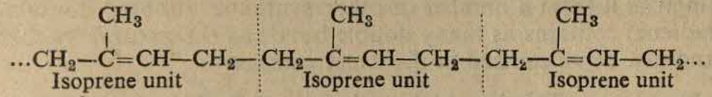
$$\underset{\text{2-Methyl 2-4-dichlorobutane}}{(CH_3)_2CCl.CH_2.CH_2CH_2Cl} \xrightarrow[-HCl]{\text{Soda-lime at } 470^\circ} \underset{\text{Isoprene}}{H_2C=C(CH_3).CH=CH_2}$$

Isoprene is a liquid boiling at 37°C. Like other compounds containing a **conjugated system of double bonds**, it undergoes 1 : 4 addition with two monovalent atoms or groups. When kept in a sealed tube at the ordinary temperature, isoprene polymerizes to a material similar to natural rubber. The process can be hastened by heating with acetic acid or metallic sodium. The **artificial rubber** thus obtained can be vulcanized and used in the manufacture of articles that are commonly made of rubber. **Butadiene**, $H_2C=CH.CH=CH_2$, 2, 3-dimethylbutadiene, $H_2C=C(CH_3).C(CH_3)=CH_2$, and other similar hydrocarbons give more or less similar polymerization products.

14. Natural Rubber.—The *latex* of the rubber tree *Hevea brasiliensis*) consists of an aqueous emulsion of a hydrocarbon of high molecular weight called **caoutchouc.** When an incision is made that penetrates the outer bark, the latex oozes out. This is treated with very dilute acetic acid to coagulate the rubber. A cheeselike coagulum separates, and is passed through rollers to produce thin sheets of "*pale crepe*" rubber. Alternatively the coagulum is milled into ribbed sheets and smoked ; the product is called "*smoked sheet*" rubber. The crude rubber, thus obtained, consists of 90 to 95 per cent of caoutchouc, about 3 per cent of fatty acids and small quantities of sugars, resins and proteins.

Crude rubber has certain objectionable characters. It is soft, sticky and gummy (plastic), and, in contact with organic solvents, swells and ultimately dissolves. To make it serviceable, the rubber must be submitted to a process known as "**vulcanization.**" This, in modern practice, consists in immersing the crude rubber in a solution of sulphur monochloride in carbon disulphide. After being vulcanized, the physical characters of rubber are improved to a remarkable extent. The tensile strength of the material becomes considerably higher and it shows elasticity over a wide range of temperature. Further, in contact with organic solvents, it does not swell to any appreciable extent and retains its original form.

The rubber hydrocarbon has been shown to be a **high polymer of isoprene**, there being 200 to 4,000 C_5H_8 units combined together in a long chain, the actual size depending on the previous treatment of raw rubber. Ozonolysis of the hydrocarbon shows that the isoprene units are joined together in the following way.



$$\ldots\underset{\text{Isoprene unit}}{CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2}-\underset{\text{Isoprene unit}}{CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2}-\underset{\text{Isoprene unit}}{CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2}\ldots$$

The process of vulcanization introduces, here and there, along the whole length of the hydrocarbon chains, **cross links** at positions of the double bonds to give a three-dimensional network. These cross links may be from carbon to carbon, or may involve a sulphur atom, or both. They prevent slipping of the hydrocarbon chains and serve to pull them back to their normal curled-up state on the removal of the stretching force. Vulcanization, therefore, considerably improves the tensile strength and elasticity of rubber. Further, on account of the saturated nature of the vulcanized product, liability of rubber for air oxidation, and consequent deterioration or "*aging*", is almost completely prevented.

15. Synthetic Rubbers.—The term "synthetic" rubber is employed for certain rubberlike **(elastoplastic)** materials which may be synthesised and used in place of natural rubber for various purposes, especially in the manufacture of automobile tyres (which is the largest single use of rubber). Quite a number of such rubber substitutes have been developed, especially during the Second World War, when all the warring countries, except Japan, were deprived of most of their sources of natural rubber. These substitutes are "high polymers" of various substances, but none of them is chemically identical with natural rubber.

16. Butyl Rubber.—We have seen that polyisobutene (sec. 10) has the properties of unvulcanized natural rubber, but cannot be used as a rubber substitute on account of the fact that it cannot be vulcanized. This drawback has been remedied by mixing isobutylene with a *small* proportion of *isoprene*, and submitting the *mixture* to polymerization. Such a reaction, where two or more substances are together submitted to polymerization with a view to developing desirable properties, is called **copolymerization**, and the product a **copolymer.** Copolymers are not merely mechanical mixtures ; the second component is *actually incorporated into the chains.* The copolymer of butylene and isoprene, called "Butyl Rubber" is prepared by adding to the mixture of the two hydrocarbons a suitable catalyst (aluminium chloride) at a low temperature (below −50°). It is the isoprene component of butyl rubber that provides a certain amount of unsaturation and consequently the property of being vulcanized. Butyl rubber vulcanizates show good resistance to aging and chemical action, and, further, their tensile strength and elasticity are higher than those of natural rubber.

17. Buna Rubber.—This is a copolymer of butadiene and styrene (vinylbenzene, $CH_2=CH.C_6H_5$), the former being in large excess.

(75 per cent). An emulsion of the two hydrocarbons in water is prepared in the presence of a suitable emulsifier and heated under pressure with a catalyst (a peroxide). The product, called[1] **Buna S** (to distinguish it from a number of other synthetic rubbers containing butadiene) contains as many double bonds as the natural rubber itself, and can be vulcanized in the usual manner.

18. Neoprene.—This is a high polymer of 2-chlorobutadiene or **chloroprene**, $CH_2{=}CCl{-}CH{=}CH_2$. It was the first synthetic rubber to be prepared in America. Chloroprene is made from acetylene in two steps. First, acetylene is treated with an aqueous solution of a copper salt as catalyst, when a *dimer*, called **vinylacetylene** is produced :

$$2CH{\equiv}CH \longrightarrow \underset{\text{Vinylacetylene}}{CH{\equiv}C{-}CH{=}CH_2}$$

The vinylacetylene is then treated with hydrochloric acid gas, when chloroprene results :

$$CH{\equiv}C{-}CH{=}CH_2 + HCl \rightarrow \underset{\text{Chloroprene (b. p., 60°)}}{CH_2{=}CCl{-}CH{=}CH_2}$$

Chloroprene polymerizes readily at room temperature, no catalyst being necessary. The process is carried out in two steps. The partially polymerized product, obtained during the first stage, has the properties of natural rubber. This is mixed with fillers and colouring materials in the same way as natural rubber, and the material is heated at 100°, when polymerization proceeds further and a product, having the characters of vulcanized rubber, is obtained.

In certain ways, neoprene is distinctly superior to vulcanized natural rubber. It is far more resistant to oils (solvent action), heat and oxidizing agents and is less permeable to gases. Hence, in spite of its relatively high cost, neoprene finds many industrial uses, such as the making of transmission belts, printing rollers and flexible tubing for the conveyance of oils and petrol.

19. Polysulphide Rubber or "Thiokol".—This is a rubber-like material obtained by heating ethylene dichloride and sodium polysulphide. Since it contains no ethylenic bonds, it is very resistant to attack by oxygen. Its most valuable property is its resistance to swelling by solvents and to abrasion. It is, therefore, used as a coating to conserve tyre tread.

ACETYLENE HYDROCARBONS OR ALKYNES

20. General Formula.—Acetylene hydrocarbons or *alkynes* contain **a triple bond** in the molecule, and their general formula is C_nH_{2n-2}. Hydrocarbons containing two or three triple bonds are called **di-** and **tri-alkynes** respectively, and their general formulae are C_nH_{2n-4} and C_nH_{2n-6}.

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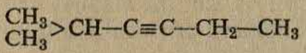
[1] Bu for butadiene, Na for sodium (which was the polymerizing agent used in the original process) and S for styrene.

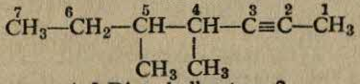
21. Nomenclature.—The same two methods are employed for naming acetylene hydrocarbons as described for elefins. In the first method, the higher homologues are regarded as derived from the first member of the series *viz.*, acetylene, HC≡CH. Thus, the alkyne having the structure



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-C\equiv C-CH_2-CH_3$$

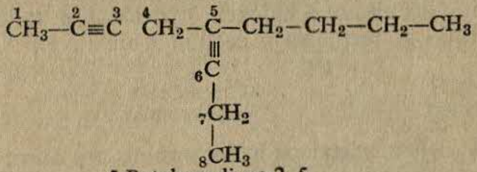
is called *ethylispropylacetylene.*

Geneva System.—In the Geneva System, the suffix *-ine* was formerly used to designate the series, but at the **Liege conference of IUC**, held in 1930, it was agreed to replace it by **-yne**, as the suffix *-ine* is also employed for names of organic bases and alkaloids (*e.g.*, pyridine, quinoline, coniine, quinine, etc.). The rest of the conventions are the same as for alkenes. In naming an alkyne, or a dialkyne, we must, of course, select the longest chain *containing the triple bond or bonds.* The following examples illustrate the system :



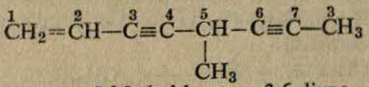
$$\overset{7}{C}H_3-\overset{6}{C}H_2-\underset{CH_3}{\underset{|}{\overset{5}{C}H}}-\underset{CH_3}{\underset{|}{\overset{4}{C}H}}-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_3$$

4, 5-Dimethylheptyne-2



$$\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}\ \overset{4}{C}H_2-\begin{matrix}\overset{5}{C}\\ \|| \\ {}_6C\\ | \\ {}_7CH_2\\ | \\ {}_8CH_3\end{matrix}-CH_2-CH_2-CH_2-CH_3$$

5-Butyloctadiyne-2, 5



$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}\equiv\overset{4}{C}-\underset{CH_3}{\underset{|}{\overset{5}{C}H}}-\overset{6}{C}\equiv\overset{7}{C}-\overset{3}{C}H_3$$

5-Methyl-l-octene-3,6-diyne

22. General Methods of Formation.—Alkynes are obtained from the following sources :—

(1) From the *dihalogen addition products of alkenes*, by the withdrawal of two molecules of halogen hydride ; *e.g.*,

$$\underset{\text{Ethylene dibromide}}{CH_2Br.CH_2Br}\ \xrightarrow{-2HBr}\ \underset{\text{Acetylene}}{CH\equiv CH}$$

The elimination of halogen hydride is effected by heating with alcoholic potash, or better, with alcoholic potassium ethoxide.

(2) From *aldehydes* and *ketones*, by first converting them into dichloro-paraffins by treatment with phosphorus pentachloride, and then heating the dichloro-derivatives with alcoholic potash, *e.g.*,

$$\underset{\text{Acetaldehyde}}{CH_3CHO}\ \xrightarrow{PCl_5}\ \underset{\text{1,1-Dichloroethane}}{CH_3.CHCl_2}\ \xrightarrow{-2HCl}\ \underset{\text{Acetylene}}{HC\equiv CH}$$

$$\underset{\text{Acetone}}{CH_3.CO\ CH_3}\ \xrightarrow{PCl_5}\ \underset{\text{2,2-Dichloropropane}}{CH_3.CCl_2\ CH_3}\ \xrightarrow{-2HCl}\ \underset{\text{Propyne}}{CH_3.C\equiv CH}$$

(3) From *complex organic substances*, by dry distillation. The presence of acetylene in coal gas is due to this cause.

23. Properties. *Physical.* The members of the acetylene series up to $C_{12}H_{22}$ are gases or volatile liquids with a peculiar odour. The higher members are solids. Like the alkanes and the alkenes, they are readily soluble in alcohol and practically insoluble in water.

Chemical. The chemical reactions of alkynes may be divided into three groups :

(1) **Addition.** Since these hydrocarbons contain a triple bond, they can combine with *four* monovalent atoms or groups. The combination with hydrogen, halogens, and halogen hydrides takes place in *two stages*, each of which corresponds to the addition of one molecule of the reagent ; *e.g.*,

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+ H_2} \underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{+ H_2} \underset{\text{Ethane}}{CH_3.CH_3}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+ Br_2} \underset{\text{Acetylene dibromide}}{CHBr{=}CHBr} \xrightarrow{+ Br_2} \underset{\text{Acetylene tetrabromide}}{CHBr_2.CHBr_2}$$

When two molecules of a halogen hydride are taken up, both the halogen atoms go to the *same* carbon atom[1] ; *e.g.*,

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+ HBr} \underset{\text{Vinyl bromide}}{CH_2{=}CHBr} \xrightarrow{+ HBr} \underset{\text{Ethylidene bromide}}{CH_3.CHBr_2}$$

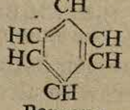
Like the olefins, acetylene hydrocarbons are absorbed by sulphuric acid. When the solution is diluted with water, and then distilled, an aldehyde or a ketone passes over. Thus the final result is the addition of a molecule of water.

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

$$\underset{\text{Methylacetylene}}{CH_3.C{\equiv}CH} + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

(2) **Polymerization**[2]. Under certain conditions, alkynes undergo polymerization. Thus, when acetylene is heated at a dull-red heat it is converted into benzene :—

$$\underset{\text{Acetylene}}{3CH{\equiv}CH} \longrightarrow$$



Benzene

Similarly, methylacetylene and dimethylacetylene, when treated with concentrated sulphuric acid, yield mesitylene and hexamethylbenzene respectively.

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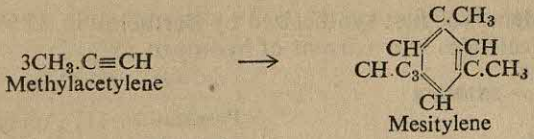
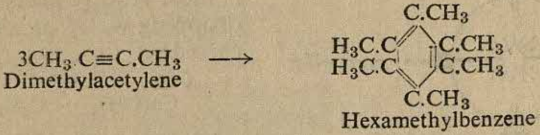
[1] This is in accordance with the Markownikoff rule.

[2] The term *Polymerization* refers to a chemical reaction involving the direct union of two or more molecules of a substance to form a new compound, whose molecular weight is a multiple of that of the original substance.


$3CH_3.C{\equiv}CH$ Methylacetylene → Mesitylene


$3CH_3.C{\equiv}C.CH_3$ Dimethylacetylene → Hexamethylbenzene

Polymerization of alkynes is an important **method of passing from the aliphatic to the aromatic compounds.**

Another important polymerization reaction of acetylene is its conversion into Neoprene (Sec. 18, p. 168).

(3) **Formation of Metallic Derivatives.** A very characteristic property of acetylene and its monalkyl derivatives, $R.C{\equiv}CH$, is the power of forming precipitates with ammoniacal solutions of silver nitrate and cuprous chloride. Thus, when acetylene is passed through an ammoniacal solution of silver nitrate, it produces a white precipitate of **Silver Acetylide**, C_2Ag_2 :

$$\begin{array}{l} C_2H_2 + 2AgNO_3 \rightleftharpoons C_2Ag_2 + 2HNO_3 \\ \underline{HNO_3 + NH_4OH \text{ —— } NH_4NO_3 + H_2O} \qquad [\times 2] \\ C_2H_2 + 2AgNO_3 + 2NH_4OH \longrightarrow C_2Ag_2 + 2NH_4NO_3 + 2H_2O \end{array}$$

Similarly, with an ammoniacal solution of cuprous chloride a brown-red precipitate **of Cuprous Acetylide**, C_2Cu_2, is produced. Both these compounds are explosive, silver acetylide being more so than the cuprous compound.

The formation of the acetylide precipitates is used as a **distinctive test** for acetylene and its monoalkyl derivatives. Further, since the precipitates regenerate the original hydrocarbon on warming with hydrochloric acid, their formation is utilized for the **purification of alkynes of this particular class** and also for their **separation** from all other hydrocarbons.

When acetylene, or one of its monalkyl derivatives, is passed over heated sodium or potassium, hydrogen is set free, and metallic substitution products, such as C_2HNa, and C_2Na_2, are formed.

The dialkyl acetylenes do *not* form metallic derivatives of the above type, since they contain no hydrogen in direct combination with the triply bound carbon atoms.

24. Acetylene, *Ethyne*, CH≡CH.

Occurrence. Acetylene occurs in coal-gas to the extent of about 0·06 per cent. When a Bunsen burner strikes back, the gases formed contain up to 0·8 per cent of acetylene (see Expt. 5).

Synthesis. Acetylene was first synthesized by Berthelot in 1859 by sparking carbon electrodes in a current of hydrogen (Fig. 2).

$$2C+H_2 \longrightarrow C_2H_2$$

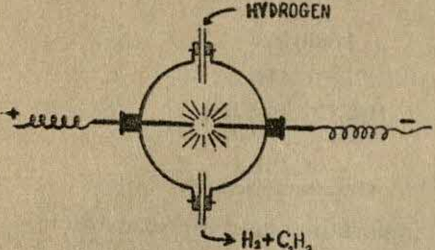


Fig. 2. Berthelot's synthesis of acetylene.

Preparation. (1) Acetylene is most readily prepared by dropping water on calcium carbide[1] :

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

The gas evolved from the commercial carbide is contaminated with ammonia, hydrogen sulphide and phosphine. It may be washed with an *acid* solution of cupric sulphate, which removes all the above impurities.

Expt. 4. Fit up the apparatus shown in Fig. 3. Place a layer of sand in the filtering flask, and cover this with a few pieces of calcium carbide. Place a solution of cupric sulphate acidified with hydrochloric acid in the Drechsel bottle. Admit water, dropwise, through the dropping funnel, and collect the evolved gas over water.

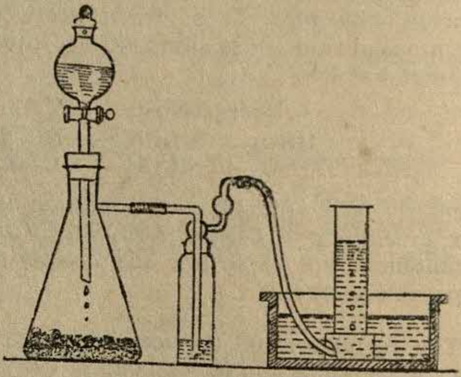


Fig. 3. Preparation of Acetylene from Calcium Carbide.

(2) An important new method for preparing acetylene on a commercial scale is by pyrolysis of natural gas.

(3) The formation of acetylene during incomplete combustion of coal gas or ether may be shown by means of the following experiments :

Expt. 5. Light a Bunsen burner at the base, and asspirate the resulting gases through a Drechsel bottle containing some ammoniacal cuprous chloride solution. It will be observed that a reddish brown precipitate of cuprous acetylide is formed (Fig. 4).

Expt. 6. Pour some ammoniacal solution of cuprous chloride into a wide boiling-tube, and then a little ether. Light the ether at the mouth of the tube, and, while it is burning, hold the tube in slanting position and give it a slow rotatory motion. It will be observed that a precipitate of cuprous acetylide is formed in this case also.

(4) Acetylene is also formed when a solution of sodium or potassium salt of fumaric or maleic acid is submitted to electrolysis.

---

[1] This reaction proves that calcium carbide possesses the structure of a true acetylide, $Ca^{++}[C\equiv C]^{--}$.

The reaction consists in the **oxidation of the anion of the salt** at the anode[1] :—

$$\begin{array}{c}\text{CHCOO}^-\\ \|\\ \text{CHCOO}^-\end{array} \xrightarrow[-2e^-]{\text{anodic oxidation}} \begin{array}{c}\text{CH}\\ |||\\ \text{CH}\end{array} + 2CO_2$$

Physical Properties. Acetylene is a colourless gas, which, when pure, has a peculiar ethereal smell. The objectionable odour of the gas prepared from the commercial carbide is due to impurities, especially phosphine. Water dissolves about 1 volume, alcohol 6 volumes, and acetone 25 volumes of the gas under the ordinary conditions.

Caution. Acetylene cannot be safely stored under a pressure greater than 2 atmospheres, as it is then **liable to explode violently by mere shock.** In storing acetylene, advantage is sometimes taken of the fact that acetone can dissolve 300 volumes of the gas under a pressure of 12 atmospheres. It is in the form of acetone solution (which, unlike gaseous acetylene, is not liable to explode) that acetylene is transported in steel cylinders, when required for welding, cutting steel, etc.

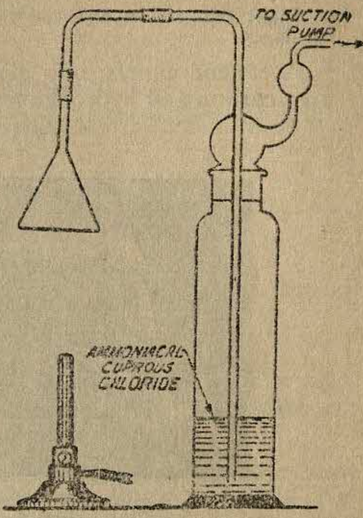


Fig. 4. Formation of acetylene during incomplete combustion of coal gas.

Chemical Properties. (1) Acetylene is an endothermic and unstable compound. When submitted to a pressure of more than 2 atmospheres and detonated, it decomposes into its elements with explosive violence :

$$C_2H_2 \longrightarrow 2C + H_2$$

(2) Acetylene burns with a luminous, smoky flame. When burnt from a jet with a very fine aperture, the flame is not smoky but exceedingly luminous. In an **acetylene burner**, the gas issues from two small openings so arranged that the two fine streams of gas strike against each other to produce a flat flame. Side-holes are provided through which air is sucked in and gets mixed with the gas as it rushes through the nozzle. The result is a flame that is non-smoky and highly luminous.

The oxy-acetylene blowpipe (Fig. 5) gives the hottest of all flames (temp.=2,700°), and is used for welding, cutting and making holes into steel plates.

Like all hydrocarbons, acetylene forms an explosive mixture with air.

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[1] Compare the formation of ethylene from an alkali succinate.

Expt. 7. Light some acetylene contained in a glass-cylinder. It burns with a smoky flame.

Light the gas in an acetylene burner. Notice that the flame is of dazzling brilliancy.

Acetylene bursts into flame in contact with chlorine, producing free carbon and hydrochloric acid gas :—

$$C_2H_2 + Cl_2 \longrightarrow 2C + 2HCl$$

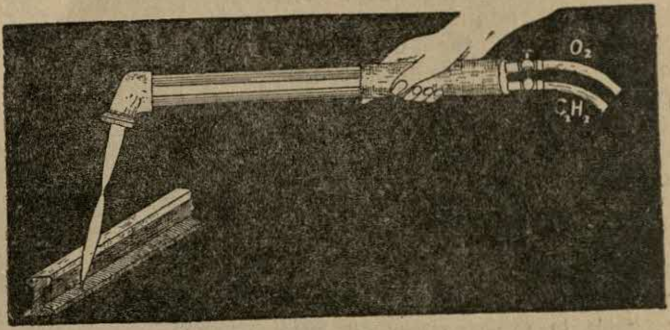

Fig. 5. Oxy-acetylene Torch.

Expt. 8. (*a*) Place a cylinder containing acetylene over another containing chlorine. Notice that the mixture ignites *spontaneously*, with the deposition of carbon and formation of fumes of hydrogen chloride.

(*b*) Throw a small piece of calcium carbide into a trough containing water, and bring the end of the delivery tube of a chlorine generator near the bubbles of acetylene as they rise from water ; notice that the bubbles of the gas ignite spontaneously.

(*c*) Pour some ammoniacal silver nitrate solution into a cylinder full of acetylene. Notice that a white precipitate of silver acetylide is formed.

(*d*) Pour some ammoniacal cuprous chloride solution into another cylinder of acetylene. Notice the formation of a red-brown precipitate of cuprous acetylide.

(3) Acetylene shows all the characteristic reactions of the hydrocarbons of this series (sec. 23). When it is passed into warm, 20 per cent sulphuric acid, containing a little mercuric sulphate, it adds on a molecule of water, yielding acetaldehyde.

$$CH{\equiv}CH + H_2O \longrightarrow CH_3CHO$$

This reaction is of considerable commercial importance.

Uses. (1) As already stated, acetylene is used as an illuminant and in the oxy-acetylene torch.

(2) Acetylene, carefully purified from all impurities, is used as an anaesthetic under the name **Narcylen.**

(3) Acetylene is a *synthetic agent* of great importance. It can be readily obtained from its elements, and is very reactive. These two facts make acetylene almost indispensable in a large number of "complete syntheses" of organic substances. The advent of cheap electric energy, derived mainly from water-power, has made it possible

to produce calcium carbide, and, therefore; acetylene, very cheaply. Hence, the possibilities of utilizing acetylene for the manufacture of organic substances of economic value have recently attracted much attention.

The most important **synthetic uses** of acetylene are :

(*e*) Conversion of acetylene into *acetaldehyde* which in turn yields:

(*i*) *ethyl alcohol*, by reduction,

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

(*ii*) *acetic acid*, by oxidation,

$$CH_3CHO + O \longrightarrow CH_3COOH$$

(*iii*) *ethyl acetate*, by polymerization in the presence of aluminium ethoxide,

$$2CH_3CHO \longrightarrow CH_3COOC_2H_5$$

In addition to above three compounds, a number of other important aliphatic compounds of simple constitution have been obtained from acetylene, *via* acetaldehyde.

(*b*) Conversion of acetylene into *benzene* at a dull red heat may some day prove to be of great commercial importance, though so far it cannot be said to possess any practical significance.

(*c*) Conversion of acetylene into **vinylacetylene** is the basis of the synthetic rubber, Neoprene (page 168, sec. 18).

(*d*) Conversion of acetylene into heterocyclic compounds, *thiophene* and *pyrrole*.

(*e*) Combination of acetylene with chlorine in the presence of a catalyst yields *acetylene tetrachloride*, $C_2H_2Cl_4$, which is used extensively as a solvent under the name **westron**. The latter is also employed in the preparation of other solvents: *e.g.*, *westrosol* (trichlorethylene), $CCl_2{=}CHCl$, and *acetylene dichloride* $CHCl{=}CHCl$.

(*f*) Acetylene finds an important application in the manufacture of the war gas **Lewisite.**

(4) Acetylene is also used for the manufacture of hydrogen. The process consists in decomposing acetylene contained in steel cylinders by electric sparks. The very fine carbon obtained as the by-product is used for making printer's ink.

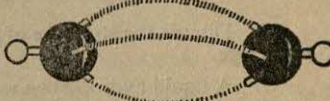

Fig. 6.

Constitution. The constitution of acetylene follows from its formation from ethylene dibromide and acetaldehyde (sec. 22), the two carbon atoms being linked together by a triple bond. The representation of the molecule by atomic models is shown in Fig. 6.

25. Homologues of Acetylene.—The homologues of acetylene are divided into two distinct classes, *viz.*, mono-alkyl acetylenes and di-alkyl acetylene. As already mentioned, the former class gives mono-metallic substitution compounds, while the latter are incapable of yielding such derivatives.

Propyne, *methylacetylene*, $CH_3.C{\equiv}CH$, is a gas readily condensible to a liquid boiling at *minus* 24°. When treated with concentrated sulphuric acid it yields mesitylene (page 171).

Butyne, C_4H_6, exists in two isomeric forms *viz.*,

$CH_3.CH_2.C{\equiv}CH$	and	$CH_3.C{\equiv}C.CH_3$
Butyne-1 or ethylacetylene		Butyne-2 or dimethylacetylene

25. Diacetylenes.—The diacetylenes contain two triple bonds, and have the general formula C_nH_{2n-6}, which is identical with that of the benzene hydrocarbons. In chemical behaviour, the hydrocarbons of this series resemble acetylenes, and combine with four monovalent atoms or groups. They polymerize with great ease.

Diacetylene, *butadiyne*, $CH{\equiv}C-C{\equiv}CH$, is a gas of a peculiar odour. It can be readily converted into a liquid which boils at 10°. It yields a violet-red copper compound and a yellow silver compound, the latter exploding on being rubbed, even when moist.

Dipropargyl[1], **1,5-***Hexadiyne* $CH{\equiv}C.CH_2.CH_2.C{\equiv}CH$, possesses a special interest, as it is isomeric with benzene, C_6H_6.

QUESTIONS

1. Tell why the following names are objectionable, and give a suitable name (I.U.C.) to each :—

(*i*) 4-Methylpentane, (*ii*) Methylisopropylmethane, (*iii*) 2-Methyl-3-hexane, (*iv*) 3-Methyl-4-heptene (*v*) 2,2,4-trimethyl-3-pentane.

(*Lucknow, B.Sc., 1961*)

2. Enumerate and discuss the various methods available for the preparation of ethylene compounds.

Discuss the ordinary method of representing a double bond and point out its defects. How does Baeyer's Strain Theory attempt to explain unsaturation in organic compounds ? (*Punjab, B.Sc., 1943*)

3. How would you prepare ethylene in the laboratory ? How does it react with (*a*) bromine-water, (*b*) conc. sulphuric acid, (*c*) hydrogen chloride, and (*d*) acidified potassium permanganate ? (*Madras, B.Sc., 1941*)

4. Describe the method employed for the detection and estimation of the ethylenic group. (*Punjab, B.Sc., 1939*)

5. 12 ml. of a gaseous hydrocarbon were mixed with 90 ml, of oxygen and the mixture exploded. After explosion, the volume was 72 ml. On adding KOH, 36 ml. of gas disappeared, leaving oxygen only. What is the molecular formula of the gas ? All the above measurements were made at 15°C and 775 mm. pressure, the gases being saturated with moisture. [Aq. tension, at 15°C=12·7mm].

(*Ans.* C_3H_6)

6. Discuss the structure of ethylene, giving all the evidence for its accepted structure. (*Rajasthan, B.Sc., 1961*)

7. A liquid hydrocarbon was found to contain 85·7 per cent of carbon. Its vapour density was 35. It decolorized dilute alkaline potassium permanganate solution and bromine water. When treated with ozone and dilute hydrochloric acid, it gave both acetaldehyde and acetone. What hydrocarbon was it.

Ans. Trimethylethylene, $(CH_3)_2C{=}CH.CH_3$.

8. Give the structure formulae, names (I.U.C.) and the methods of identification of the isomeric butenes. (*Lucknow, B.Sc., 1962*)

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[1] The monovalent group, $CH{\equiv}C.CH_2-$, derived from propyne, $CH{\equiv}C.CH_3$, is termed *propynyl* or *propargyl.*

9. A hydrocarbon, C_5H_{10}, yields 2-methylbutane on catalytic hydrogenation and adds HBr to form a compound that on reaction with silver hydroxide affords an alcohol. The latter on oxidation gives a ketone. What is the structure of the hydrocarbon? (*Lucknow, B.Sc., 1959*)

10. How is double bond detected and its position in a carbon chain located? Discuss the addition of Cl_2, Br_2, I_2, HCl, HBr and HI to propylene. (*Bombay, B.Sc., Chemistry, Subs., 1963*)

11. Outline two methods for the preparation of propylene in the laboratory. Indicate how this hydrocarbon reacts with (*a*) bromine, (*b*) hypochlorous acid, (*c*) sulphuric acid, and (*d*) hydrobromic acid. (*Osmania, B.Sc., 1954*)

12. Give the structural formulae of the isomeric Butenes and describe the methods of synthesising them. Mention the products that are obtained by their ozonolysis. (*Lucknow, B.Sc., 1956 ; Gorakhpur, B.Sc., 1962*)

13. Discuss the structure of ethylene, giving all evidence for its accepted structure. (*Ajmer, B.Sc., 1961*)

14. Describe the laboratory preparation of ethylene. Compare the properties of ethylene with those of acetylene. (*Venkateswara, B.Sc., 1961*)

15. How is ethylene prepared in the laboratory? Compare and contrast its properties with those of ethane. (*Annamalai, B.Sc., 1962*)

16. What happens when :

(*a*) Acetylene is passed through ammoniacal silver nitrate solution ;
(*b*) Propylene is treated with Hydrobromic acid ;
(*c*) Ethylene reacts with concentrated Sulphuric acid ;
(*d*) Propylene reacts with Hypochlorous acid ;
(*e*) Acetylene is passed through a red hot tube. (*Saugar, B. Sc., 1962*)

17. Describe clearly the meaning of the terms *Unsaturation* and *Double Bond.* Give the tests that you would perform to ascertain unsaturation in ethylene. (*Patna, B.Sc., 1959*)

18. What are the general methods of preparation of acetylenic compounds and what are their characteristic properties? What explanation would you offer for their great instability? Describe the synthetic and industrial uses of acetylene. (*Punjab, B.Sc., 1950*)

19. A hydrocarbon was found to contain C, 88·9 per cent ; H, 11·1 per cent. On being treated with excess of bromine it gave a compound containing 79·3 per cent of bromine. With ammoniacal silver nitrate solution it gave a white precipitate. What hydrocarbon was it? *Ans.* Ethylacetylene, $CH_3.CH_2.C{\equiv}CH$.

20. How is acetylene prepared? State its properties and uses. Explain how you convert acetylene into methane, ethylene and benzene respectively. (*Andhra, B.Sc., Subsidiary, 1954*)

21. (*a*) Give the general methods of preparation and properties of Acetylenic compounds.
(*b*) Describe the synthetic and industrial uses of Acetylene. (*Jammu & Kashmir, B.Sc., 1954*)

22. Give an account of the preparation of unsaturated hydrocarbons and discuss their characteristic reactions. (*Utkal, B.Sc., 1955*)

23. How is acetylene prepared in the laboratory? What happens when acetylene is treated with (*a*) hydrobromic acid, (*b*) dilute sulphuric acid and mercuric sulphate, (*c*) ammoniacal cuprous chloride? What commercially important compounds can be obtained from acetylene? (*Rangoon, B.Sc., 1956*)

24. What are the general methods for the preparation of unsaturated aliphatic hydrocarbons? Indicate how they differ from the paraffins in their reactions? (*Calcutta, B.Sc., 1956*)

25. Compare the properties of ethylene and acetylene. Write a note on the industrial importance of acetylene. *(Travancore, B.Sc., 1956)*

26. Write short notes on any three of the following :—

(*a*) Knocking ; (*b*) Octane number ; (*c*) Reforming ; (*d*) Aviation Petrol ; (*e*) Petrol substitutes. *(Lucknow, B.Sc., 1959)*

27. A hydrocarbon containing 88 9 per cent of carbon was found to give no precipitate with ammoniacal solutions of silver nitrate and cuprous chloride. When its solution in concentrated sulphuric acid was diluted with water and distilled, methyl ethyl ketone passed over. The vapour density of the hydrocarbon was 27. What hydrocarbon was it ? *Ans.* Dimethylacetylene. $CH_3.C{\equiv}C.CH_3$.

28. Give the industrial preparation of acetylene. Name the products and give the equations when (*a*) ethylene and (*b*) acetylene are separately allowed to react with (*i*) chlorine, (*ii*) hypochlorous acid, (*iii*) sulphuric acid and (*iv*) ozone. *(Gujarat, B Sc., 1960)*

29. What are the various methods to prepare acetylene ? How will you obtain the following from it :—

(*a*) Ethene ; (*b*) Benzene ; (*c*) Acetaldehyde ? *(Saugar, B.Sc., 1961)*

30. Compare and contrast the properties of ethylene with those of acetylene. How could you convert acetylene into (*a*) acetaldehyde ; (*b*) tetrachloroethane and (*c*) *n*-butyl alcohol ? *(Calcutta, B.Sc., 1962)*

31. Give the synthetic uses of acetylene. *(Lucknow, B.Sc., 1962)*

32. State the Markonikoff rule. Give equations to illustrate its applications. *(Lucknow, B.Sc., 1962)*

CHAPTER ELEVEN

PETROLEUM INDUSTRY

1. **Occurrence of Petroleum.**—Huge quantities of complex mixtures of hydrocarbons occur under the earth's crust as "**Petroleum.**" The total annual world production of petroleum is about 1,000,000,000 barrels (1 barrel=42 gallons). About 60 per cent of the world's supply comes from U.S.A. Other petroleum producing countries in the order of production are : U.S.S.R., Venezuela (South America), Iran, Rumania, Mexico, Iraq, Poland, Burma and India.

The oil fields of India all lie in the north-east corner of the State of Assam. The most important of these is the **Digboi oil-field** with its 1,000 wells, which is one of the oldest producing fields of the world. The **Digboi refinery** was the first refinery set up in India, and is now a modern full-scale plant owned by the Assam Oil Company.

The search for new sources of oil beyond Digboi ultimately led to the discovery of oil at Nahorkatiya (1953), Hugrijan and Moran in the alluvial valley of Brahamputra. The reserves of oil in these fields are sufficient to yield more than two and a half million tons a year. A new oil company, **Oil India Limited** (O.I.L.), has been formed with Indian and British capital to develop these rich resources of Petroleum.

The quantity of oil from Assam, though considerably increased in recent

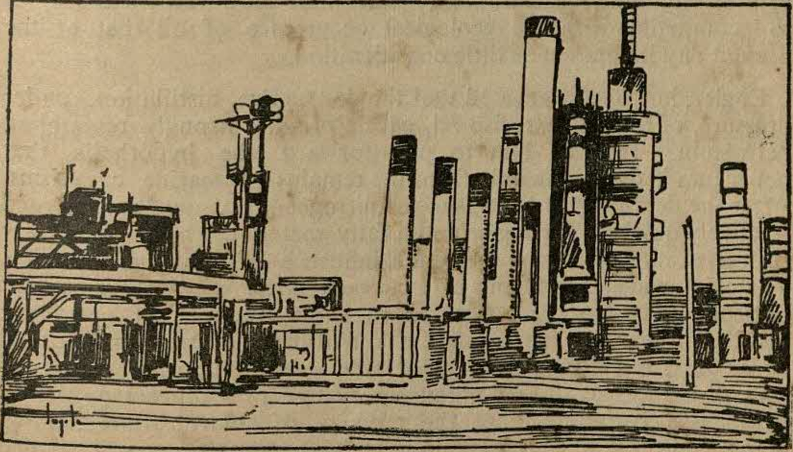


Fig. 1. A view of Caltex Oil Refining (India) Ltd., Visakhapatnam (Andhra Pradesh). The refinery went into production in July, 1957, and is a present producing 450,000 gallons of high grade petroleum products per day.

years, is not however sufficient to meet the huge demand for petroleum in India. Hence, the Indian Government is importing crude petroleum from abroad. which is being refined in distilleries installed in our own country. Two of these refineries, one set up by Burma Shell and the other by Standard Vacuum Oil Company, are at Trombay island near the city of Bombay. A third one has been built by Caltex at Visakhapatnam.

2. **Physical Characters.**—Crude petroleum is a viscid, fluorescent liquid having a dark green, yellow or brown colour. It usually possesses an offensive odour owing to the presence of organic sulphur compounds.

3. **Composition of Petroleum.**—Petroleum consists essentially of a mixture of hydrocarbons of the paraffin series together with cycloparaffins and hydrocarbons of the aromatic series. The actual composition, however, varies with the place of origin. The Pennsylvanian oil contains about twenty different hydrocarbons, most of which are of the paraffin series. The Russian oils, on the other hand, contain a large proportion of higher-boiling aromatic hydrocarbons, together with penta- and hexa- methylenes (naphthenes). The low-boiling fractions of most petroleums consist mainly of the lower hydrocarbons of the paraffin series.

4. **Origin of Petroleum.**—Two theories have been proposed as to the origin of petroleum, one *organic* and the other *inorganic*, both being supported by experiment. The Russian chemist Mendeljeff suggested that petroleum is formed by the action of water on metallic carbides present in the hot interior of the earth. This **"inorganic" theory** of the origin of petroleum was later supported by the work of Moissan, and of Sabatier and Senderens. However, the theory is so incompatible with the geological occurrence of oil that at the present day it commands little consideration.

Engler, in 1900, discovered that the destructive distillation, under pressure, of fats, such as fish oil, gave a product strongly resembling petroleum. This led him to put forward the hypothesis that petroleum is derived mainly from the remains of marine organisms. After the death of the organism, the nitrogenons content decomposed relatively quickly ; leaving behind a fatty material which got slowly converted into petroleum under the influence of heat and pressure. The chief evidence in favour of the **organic origin of petroleum** is that optical activity has been observed in some fractions of petroleum distillation and that they contain coloured organic compounds, called *porphyrins*, related to chlorophyll (the green colouring matter of leaves) and to haemin (red colouring matter of oxygenated blood). From this it follows that the remains of chlorophyll-containing plants and those of haemoglobin-containing animals have contributed towards the formation of petroleum. Another fact that supports the organic origin of petroleum is the invariable presence in it of nitrogen and sulphur compounds.

5. **Mining of Petroleum.**—Petroleum occurs at depths which vary within very wide limits. At Virginia and Ohio, the oil strata are

from 50 to 60 feet deep ; in Pennsylvania they are from 2,400 to 2,600 feet deep. Petroleum is brought to the surface by drilling wells through the overlying strata into the oil-bearing sandstone. A section through an oil-field is shown in Fig. 2. If a boring be made in the middle, we would get only salt water. In the two positions where the wells are shown to be drilled, we would get petroleum (right) and natural gas (left).

Many wells, particularly in newly-opened territory, where the original gas-pressure has not been lost, are flowing wells, known as "gushers". This spontaneous flow, however, soon declines, when pumping becomes necessary in order to maintain the production of oil.

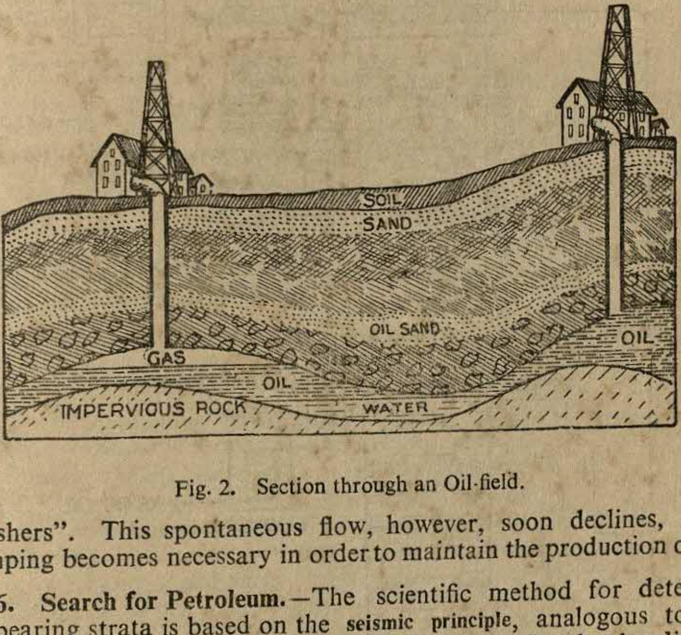


Fig. 2. Section through an Oil-field.

16. Search for Petroleum.—The scientific method for detecting oil-bearing strata is based on the **seismic principle**, analogous to the seismographic method of detecting earthquakes. In the locality to be investigated, a test hole is made, and an explosion is set off in it. The earth-tremor waves reflected from the underlying strata are recorded on a seismograph. Mathematical analysis of the seismographic curves thus obtained gives a fairly sure indication of the presence or absence of oil.

17. Distillation of Petroleum.—In modern practice, crude petrolium is submitted to fractional distillation in tall fractionating columns of the ball-and-plate type described in sec. 7, chap. 2. The distillation process, called **continuous rectification.** extends throughout the tower. The temperature of the tower falls from bottom upwards, and various fractions are taken out of the tower at different levels depending on their relative volatility.

The complete set-up of the plant is shown in Fig. 3. The crude oil enters at the upper right hand corner of the figure, and is pumped through the system as shown by arrow heads. After being preheated by the vapour coming off from the fractionating column, it passes on to the heating furnace and thence to the vaporizer. The comparatively non-volatile portion that escapes vaporization is drawn off as fuel oil at the lower right-hand corner of the figure, while the vapour is admitted into the fractionating column about the middle.

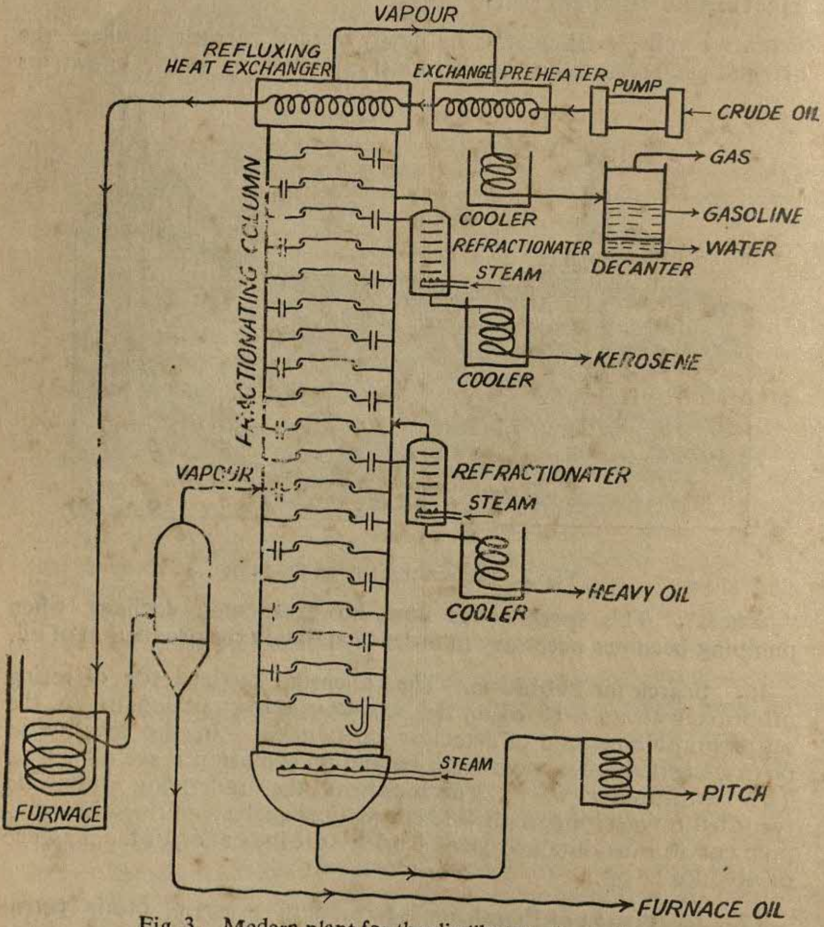


Fig. 3. Modern plant for the distillation of petroleum.

Subsidiary refractionating units are attached to the main fractionating column to give sharp fractions and for effecting further separation of components as desired.

18. Products of Petroleum Distillation.—The different products obtained in the fractionation process are described below :—

(1) **Gasoline.** This is the most volatile fraction. It is submitted to further refractionation in a subsidiary unit, and separated into :—

(*i*) *Petroleum ether* or *light petroleum* (40°—70°) ;

(*ii*) *Gasoline* or *petrol* (70°—120°) ;

(*iii*) *Ligroin* or *white spirit* (120°—150°).

While gasoline or petrol is used as fuel in motor and aeroplane engines, petroleum ether and ligroin are used as solvents of fats and oils, in dry-cleaning and for blending into fuels.

(2) **Kerosene.** This fraction (boiling up to 350°) is used as an illuminant and as fuel oil for heavy motors (Diesel oil). It is refined by treatment with concentrated sulphuric acid.

The oil is agitated with the required quantity of the acid (1·5 to 2 per cent) by a blast of cold air in a tall cylindrical tank of iron lined with sheet lead. The agitation is allowed to go on as long as action is indicated by the rise of temperature, when the black-coloured, thick acid-tar (consisting of sulpho-compounds of the olefines and other unsaturated hydrocarbons) is allowed to settle and withdrawn through a pipe attached to the bottom of the tank. After the acid treatment, the oil consists of the paraffin hydrocarbons largely freed from olefines and other hydrocarbons. It is washed with water, until the wash-water shows no acid reaction. Then about 1 per cent of sodium hydroxide solution of 12° *Be* is introduced and the mixture agitated. The waste alkali is run off, and the oil is transferred to settling tanks. Here, any water present in the oil settles out, and the oil becomes clear and brilliant.

Kerosenes to be used in lamps should not be sufficiently volatile at the ordinary temperature to form explosive mixtures with air. The *lowest temperature at which an oil gives off a sufficient amount of vapour to form an explosive mixture with air* is termed its **Flash Point.** To protect the public against the low-flash oils, which would be dangerous to use in lamps, laws have been made by different Governments, forbidding the sale of oils having flash points below a certain minimum. The minimum flash-point prescribed differs in different countries. In India, which has a hot climate, it is fixed at 44°C, while in France, which has a colder climate, a minimum flash-point of 35°C is permitted.

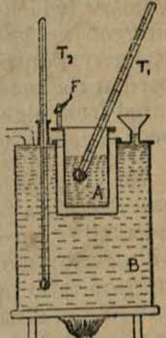


Fig. 4. Abel's flash-point apparatus.

The flash-point of an oil is usually determined by means of Abel's apparatus (Fig. 4). The sample to be tested is placed in a small, metal cup, *A*, which is gradually heated by means of the surrounding water bath, *B*. A small test flame, *F*, is lowered into the space above the oil from time to time by means of an automatic device. As soon as the vapour ignites with a minute explosion, the temperature, indicated on the thermometer, T_1, is noted. Besides this thermometer which is graduated from 10°C to 50°C, there is another one, T_2, graduated from 50° to 75°C for the water bath.

Expt. 4. Place some kerosene oil in a beaker provided with a thermometer and heated on a water bath. After every one degree rise of temperature above 30°, test the vapour inside the beaker by means of a lighted. match. The temperature at which the vapour ignites with a small explosion is taken as the *approximate* flash-point of the oil.

(3) **Heavy Oil.** This is the fraction boiling above 350°. Its composition and utilization vary according to the nature of the crude oil. Thus, Burmah and Pennsylvanian oils, that are rich in higher alkanes, give **paraffin wax** on strong cooling. This product is used in the manufacture of candles, as a seal for jams and jellies, as an impregnating agent in wax papers and in other directions.

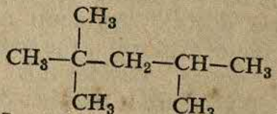
Russian, Californian and Rumanian oils that are rich in cycloparaffins (naphthenes), give various grades of **lubricating oils**, **greases** and **vaseline** (petroleum jelly). The last named is used in toilet, in making ointments, abrasive binders, printer's ink and in wood impregnation, etc.

(4) **Petroleum Asphalt or Pitch.** The heavy, dark coloured, residual oil is worked up for *petroleum asphalt* or *petroleum pitch*. This is employed in road making, waterproofing and electrical insulation.

(5) **Gas.** Uncondensed gas leaving at the top of the fractionating column is analogous in composition to *natural gas* and is treated and utilized similarly (see sec. 26).

19. Manufacture of Gasoline.—The demand for gasoline or petrol has increased considerably on account of the increase in the number of automobiles and world-wide expansion of aviation. The *natural gasoline* (which is extracted from natural gas by compression) and *straight-run gasoline* (the low-boiling fraction obtained in the Refinery) constitute only a minor proportion of the total gasoline used at the present time. Considerably larger quantities are manufactured from high-boiling fractions by a variety of processes that have been carefully worked out (sec. 23, 24).

20. Octane Number or Octane Ratings.—Before discussing gasoline manufacture, we must understand the significance of an essential feature of gaseons fuels. An internal combustion engine will develop more power and use less fuel with increase in the compression ratio up to a certain point when engine develops "**knocking**", resulting in dissipation of considerable energy. The maximum compression that can be thus attained in a given engine without any knocking taking place depends on the composition of gasoline used. The higher the compression attained, the better the fuel. The quality of a motor fuel is adjudged by its "*octane number*," which is based on the fact that **2,2,4-trimethylpentane**,



$$CH_3{-}C(CH_3)_2{-}CH_2{-}CH(CH_3){-}CH_3$$

Iso-octane (octane number = 100)

called "**iso-octane**", is one of the best fuels that detonates only at high compression. It is, therefore, taken as the standard substance and is assigned an actane number of 100. The other side of the scale is represented by *n*-**Heptane,**

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$$

n-Heptane (octane number = 10)

which is a very poor automobile fuel, as it is particularly prone to knocking. It is, therefore, arbitrarily assigned an octane number of 0. A mixture of these two hydrocarbons will have an octane number between 0 and 100 depending on the per cent of *iso-octane* that it contains. Thus a gasoline is said to have an octane number of 90 when it possesses the same knocking characteristics as a mixture of 90 per cent iso-octane and 10 per cent *n*-heptane.

The octane numbers of about a hundred pure hydrocarbons have been carefully determined with a view to studying the effect of structure on the quality of a gasoline fuel. Some of the figures are given below :—

Hydrocarbon	Octane Number
n-Haxane	26
n-Heptane	0
n-Octane	—20
Iso-octane	100
Hexene-2	78
Cyclohexane	77
Benzene	100

As the result of this study, the following conclusions have been arrived at :—

1. Straight-chain or "normal" hydrocarbons are very poor motor fuels, as they have very low octane numbers. As the carbon chain lengthens, the octane number decreases.

2. The branching in the chain causes an increase in the octane number.

3. The introduction of a double bond considerably improves the octane number. Further, the octane number increases as the position of the double bond is shifted to the centre of the molecule.

4. Cycloparaffins have much higher octane numbers than the corresponding straight-chain compounds.

5. Aromatic hydrocarbons have exceptionally high octane numbers.

21. Antiknock Compounds.—The straight-run gasolines from different oil-fields differ widely in composition and, therefore, in their octane number. After a great deal of experimentation, it was found in 1922 that the octane number of a gasoline could be greatly raised by the addition of a small proportion of **tetraethyl lead,** $(C_2H_5)_4Pb$. Gasolines leaded to the point of an octane number of 80 or more are known to the trade as **ethyl gasoline.** The amount of tetraethyl lead in motor gasoline ranges from 1 to 3 ml. per gallon, the latter quantity being the legal maximum. Aviation gasoline may be more heavily leaded. Ethyl gasoline should never be permitted to come in contact with the skin, as tetraethyl lead is poisonous.

22. Cracked Gasoline.—The cracking of heavy oils to get petrol is carried out to a very considerable extent. The economical production of petrol requires that gaseous and high molecular weight by-products be minimized by suitable control of temperature, pressure, the time allowed for cracking and the use of catalysts. There are two common types of cracking processes ; namely the **liquid-phase cracking** and the **vapour-phase cracking.**

The former type is used to a much larger extent than the latter. Here the fuel oil is heated under high pressure so as to keep the cracking stock in the liquid state, until cracking occurs. Suitable catalysts are added so as to effect the cracking at a much lower temperature and thus to obtain better yields of the volatile liquids. Among many substances, used as **catalysts** for this purpose, mention may be made of iron, copper, alumina, titanium dioxide and aluminium chloride.

In the vapour-phase process, the cracking stock is distilled and the vapours are raised to a temperature of about 600°C. Here the loss in gaseous by-products is increased, but the petrol obtained possesses a higher **anti-knock value.**

Besides the liquid-phase and the vapour-phase cracking processes originally employed, other types of cracking are now being extensively practised. The so-called **mixed-phase process** is carried out at moderate temperatures (400° to 500°) under high pressures. To secure best results, optimum conditions have got to be studied and employed for each separate petroleum fraction boiling over a narrow range of temperature.

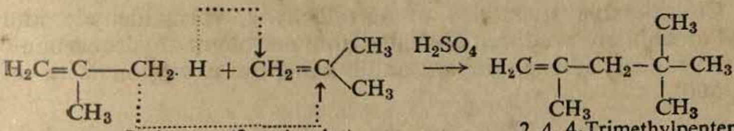
In the **catalytic cracking process,** due to Houdry (1934), a catalyst consisting of silica (4 parts), alumina (1 part) and manganese oxide (1 per cent) is employed. The **Houdry gasoline** has a high octane number (about 80), which is mainly due to the almost complete conversion of olefines into branched-chain alkanes and aromatic hydrocarbons.

A process of thermal treatment of gasolines with the specific purpose of increasing their octane ratings, called **Reforming**, consists in heating a gasoline at a high pressure for a few seconds in the presence of a catalyst (*e g.*, the Houdry catalyst). Reforming may increase the octane number by as much as 20 units, and the yield is as high as 90 to 95 per cent by volume of the charging stock.

23. Aviation Gasoline.—High-octane fuels are of great importance for commercial airplanes. In the case of fighter planes, speed and manœuvreability are of vital importance, and a 100-octane fuel is an absolute necessity.

Cracking under suitable conditions, followed by very careful fractionation, yields large quantities of ethylene, propylene, butane, isobutane and the butenes. These are valuable starting materials for the production of important chemicals and of aviation gasoline. The following processes have been utilized in the production of aviation gasoline.

(1) **Polymerization.** The first 100-octane gasoline was made in 1935 for the U.S.A. Army Air-Corps by **polymerization of isobutene** followed by the hydrogenation of the products. The conversion is carried out at moderate temperatures and pressures and in the presence of a catalyst (cold sulphuric acid). The principal product, called **iso-octene**, or *di-isobutene*, is **2,4,4-trimethylpentene-1**, and is supposed to be produced by the addition of a molecule of isobutene to the double bond of a second molecule of the olefine :



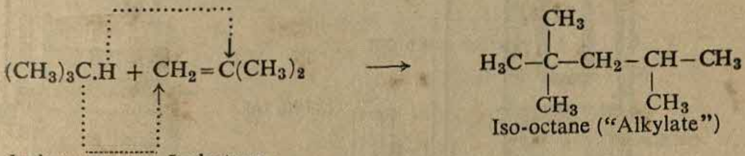
$$H_2C{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2{\cdot}H + CH_2{=}C{<}^{CH_3}_{CH_3} \xrightarrow{H_2SO_4} H_2C{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_3$$

Isobutene (2 molecules)

2, 4, 4-Trimethylpentene-1
(or iso-octene)

The second compontent of the product, constituting about 20 per cent, is the isomer 2,4,4-trimethylpentene-2. The mixture of the two olefines is then hydrogenated to an iso-octane fraction having an octane number of 91 to 97. The product is too high-boiling (91—125°) for use as aviation gasoline and is mixed with more volatile hydrocarbons.

(2) **Alkylation.** In this method, the fundamental reaction is the addition to a paraffin hydrocarbon containing a hydrogen atom attached to a *tertiary* carbon (isobutane being the only suitable gas available that fulfils this condition) to the double bond of an olefine (isobutene) in the presence of sulphuric acid or hydrogen fluoride as catalyst. The chief reaction is :



$$(CH_3)_3C.H + CH_2{=}C(CH_3)_2 \longrightarrow H_3C{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_3$$

Isobutane Isobutene

Iso-octane ("Alkylate")

The product, consisting chiefly of iso-octane, is called **"alkylate"**, and is blended with more volatile hydrocarbons, as in the first process.

(3) **Catalytic Cracking and Reforming.** These have already been described in the preceding section.

24. Petrochemicals.—A large number of organic compounds are now manufactured from petroleum and natural gas. The petrochemical industry has, is recent years, achieved a great success, and is rapidly growing. The first chemicals were made from petroleum in 1925, and the total quantity of various petrochemicals made in that year in U.S.A. was 150,000 pounds. At present, about 33 per cent of all organic chemicals are derived from petroleum or natural gas. The following are some of the more important examples of chemicals produced from petroleum.

(1) Various open-chain, saturated and unsaturated hydrocarbons produced as the result of cracking and separated by very careful fractionation.

(2) Production of iso-octane (alkylate) for use in the aviation petrol.

(3) The production of ethyl alcohol and higher alcohols from various olefin hydrocarbons obtained from petroleum.

(4) Considerable quantities of acetaldehyde, formaldehyde and methyl alcohol are produced annually from petroleum hydrocarbons, such as propene, ethane, propane and butane, by oxidation with of air at 500°.

(5) New process (1940) for the production of toluene from *n*-heptane (see under Toluene). Benzene and xylene have also been obtained. Starting from these aromatic hydrocarbons, various aromatic compounds may be obtained.

25. Oil Gas.—In making *oil gas*, a thin stream of oil is allowed to flow into a cast-iron retort heated to dull redness (Fig. 5). The cracking or pyrolysis of the liquid hydrocarbons occurs with the production of gaseous hydrocarbons, methane, ethane, ethylene, etc.

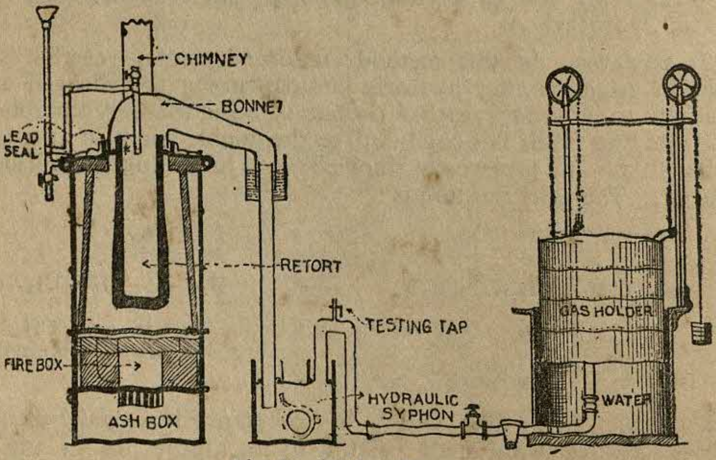


Fig. 5. Oil Gas Plant.

The gas is first passed through a scrubbing box, which retains the tarry matter present in it, and is then collected in gas-holders.

26. **Natural Gas.**—The natural gas, which comes off from the oil wells in some oil fields and in other places, consists chiefly (about 90 per cent) of methane with smaller proportions of ethane, propane, butane and isobutane and still smaller quantities of higher hydrocarbons.

Chief use of natural gas is as a fuel. It is extensively used in U.S.A. and Canada as a house-hold fuel, for raising steam in boilers and making glass and pottery. In United States alone about 90,000 miles of pipe-line is in operation for conveying natural gas to various parts of the country.

Before being delivered into the pipe-line, natural gas is generally submitted to cold and pressure with a view to condensing out propane and higher hydrocarbons. In this way **bottled gas** (to be used as household fuel in out-of-the-way places) and **natural gasoline** are obtained. The former consists chiefly of propane, while the latter consists of butanes, pentanes and hexanes.

Large quantities of natural gas is employed in the production of *carbon blacks* and *petrochemicals*.

Another use of natural gas is for the manufacture of hydrogen. The Standard Oil Company of New Jersey, U.S.A., have put up a plant capable of producing 300,000 cubic feet of hydrogen per hour. In this process, natural gas is mixed with steam and passed over a catalyst (consisting of iron or cobalt together with aluminium oxide) kept at 1,000°C, when the following reaction occurs :—

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The carbon monoxide is removed from the mixture by oxidation to carbon dioxide followed by absorption in water as in the Bosch process for the manufacture of hydrogen from water gas.

27. **Shale.**—Bituminous shale, occurring in Scotland, France and U.S.A. is an important source of liquid and solid paraffins. It is subjected to dry distillation, when ammonia, inflammable gases and shale-tar are obtained. The latter, after being washed with concentrated sulphuric acid and caustic soda, is subjected to fractionation to obtain naphtha, burning oil, lubricating oil and paraffin wax.

28. **Ozokerite.**—*Ozokerite* or *Earth wax* is often found near the surface of the ground in certain localities. Extensive deposits occur in eastern Galicia. It is a dark-coloured material, consisting of solid paraffin hydrocarbons, and is supposed to have been formed by the evaporation of shallow deposits of petroleum. It is refined by melting out from earthy impurities, and the brownish product, after being treated with concentrated sulphuric acid and alkali, is decolorized with charcoal. The purified material is used as a substitute for bees-wax under the name "**ceresin**".

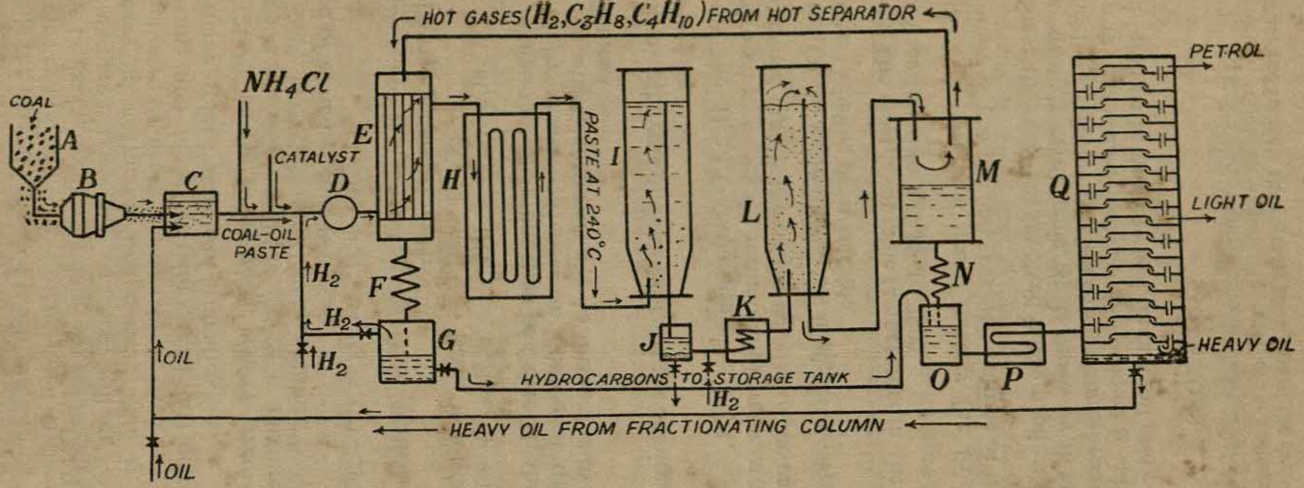
29. Synthetic Petrol.—The production of synthetic petrol is of great importance for India, as we have got almost inexhaustible deposits of coal in this country, which can with great advantage be converted into synthetic petrol.

The first attempt towards the production of liquid from solid fuel (coal) was made by Berthelot (1869), who heated finely powdered coal with hydriodic acid at 270° for several hours with a view to hydrogenating the coal. In this experiment, a liquid consisting almost entirely of hydrocarbons was obtained, the yield being about 60 per cent by weight of the coal taken. In 1913, Bergius obtained a 70 per cent yield of synthetic petroleum by heating coal with hydrogen at 450° under a pressure of 200 atmospheres. Research in the production of synthetic petroleum was continued by Tropch, Bergius, Billwiller, Bowen and others, until, in 1926, the problem assumed sufficient importance to attract the attention of the Standard Oil Company of New Jersey. At the same time, I. G. Fabin-Industri-Aktien-Gesell Schaft, under the patronage of the German Government, got interested in the problem. In 1933, the British Government, too, decided to help production of synthetic petrol, and allowed a preference of 4 pence per gallon on all synthetic petrol produced in Great Britain. Finally, the American, German, British and Dutch (Royal Dutch Shell Oil Company) interests combined together in the matter of research in this field, and their co-operative efforts have resulted in the successful development of two separate processes for the production of synthetic petrol.

(1) *Production of Synthetic Petrol by Hydrogenation of Coal* **(Bergius Process).** This process is based on the introduction of hydrogen into the complex coal molecule (empirical formula, C_2H_1) to produce a liquid similar to petrol (in which C : H ratio is 2 : 5). The process, as developed by Imperial Chemical Industries, is briefly as follows :

A paste of finely divided coal and heavy oil (the latter, from the process itself) is mixed with a small proportion of ammonium chloride (to remove alkalinity, due to coal ash, which would adversely affect the catalyst by converting the same to the oxide) and a suitable catalyst (a compound of tin—*viz.*, the chloride, sulphide or the oxalate). A sufficient quantity of compressed hydrogen (at 250 atmosphere pressure) is then incorporated. The resulting paste is heated in a preheater to 240°C, and is then admitted into a converter for **liquid-phase hydrogenation.** The paste is admitted at the base of the converter and gradually passes into the form of a liquid as the result of hydrogenation.

The liquid product from the top of the first converter is vaporized in a pipe coil heater, and a mixture of the vapour and hydrogen is admitted at the base of the second converter designed for **vapour-phase hydrogenation.** This converter is packed with a solid catalyst (granulated ZnO, MgO, MoO_3). Further hydrogenation of the oil occurs with the production of petrol with the C : H ratio 2 : 5. The vapour


HOT GASES (H_2,C_3H_8,C_4H_{10}) FROM HOT SEPARATOR
COAL
A
B
C
NH$_4$Cl
CATALYST
D
E
COAL-OIL PASTE
H_2
F
H_2
H_2
G
OIL
OIL
H
PASTE AT 240°C
I
J
K
L
M
N
O
P
Q
HYDROCARBONS TO STORAGE TANK
H_2
HEAVY OIL FROM FRACTIONATING COLUMN
PETROL
LIGHT OIL
HEAVY OIL

Fig, 6. Plant for the production of Petrol from Coal.

Parts from left to right are :—(*A*) Coal hopper. (*B*) Ball mill for grinding coal. (*C*) Mixer for making paste of coal powder and oil. (*D*) High Pressure Pump (250 atmos.) for compression of hydrogen. (*E*) Heat Exchanger where hot gases (hydrogen, C_3H_8 and C_4H_{10}) from Hot Separator, *M*, heat the coal-oil paste. (*F*) Cooling Coil. (*G*) Cold Separator in which more volatile hydrocarbons condense and are led to Storage Tank, the unused hydrogen being sent back to be reused. (*H*) Preheater for heating coal-oil-hydrogen-catalyst paste at 250 atmos. to 240°C. (*I*) Converter for liquefaction stage, where carbon and hydrogen combine to form liquid hydrocarbons. (*J*) Separator, where liquid hydrocarbon are separated from paste. (*K*) Vaporizer at 450°C to vaporize the hydrocarbons. (*L*) Converter for vapour-phase hydrogenation where hydrocarbon vapour from *K* undergo further hydrogenation in presence of a solid catalyst (granulated ZnO, MgO, MoO_3) to form petrol. (*M*) Hot Separator in which less volatile hydrocarbons condense, the hot gases (hydrogen and gaseous hydrocarbons) being let back to the Heat Exchanger, *E*. (*N*) Cooling Coil. (*O*) Storage Tank for liquid hydrocarbons. (*P*) Pipe Still. (*Q*) Fractionating Column, in which petrol, light oil and heavy oil are separated.

is led into a "hot" receiver, in which the hydrocarbons get condensed while the unused hydrogen is sent back to be mixed with the paste of fine coal, heavy oil and compressed hydrogen referred to above. The liquid hydrocarbon mixture is cooled and led to a storage tank. From here it is led on to a Pipe Still and vaporized. The vapour passes up a fractionating column, and is separated into three fractions : (*i*) heavy oil, which is re-used, (*ii*) light oils consisting of hexane and higher paraffins, and (*iii*) petrol consisting chiefly of pentane, some butane and aromatics.

(2) *Production of Synthetic Petrol from Water Gas* (**Fischer-Tropsch Process**). Water gas is a mixture of carbon monoxide (1 vol.) and hydrogen (1 vol.), obtained by passing steam through a bed of white-hot coke :—

$$H_2O + C \longrightarrow H_2 + CO - 29\ k\text{-cal}$$

The conversion of water gas into hydrocarbons is based on the following general reactions :—

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$
$$nCO + (2n + 1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

It follows that the proportion of CO to H_2 should be approximately 1 : 2 by volume. Hence, an additional quantity of hydrogen has to be added to water gas to bring the hydrogen content up to 2 volumes.

The optimum conditions for the production of petrol from water gas are :—

(*a*) The H_2 : CO ratio must be 2 : 1. A higher proportion of hydrogen increases the formation of water, while an excess of carbon monoxide rapidly lowers the activity of the catalyst.

(*b*) Of the various catalysts used, **cobalt-copper-zinc oxide** has been shown to be the most suitable.

(*c*) The most favourable temperature in the case of this catalyst has been found to be 285° to 290°.

(*d*) The optimum space velocity for this catalyst is about 120 volumes of gas per hour per unit volume of the catalyst.

Since the reactions involved in the production of synthetic petrol are strongly exothermic, it is necessary to remove the extra heat as quickly as possible by circulating water through closed pipes fitted into the reaction chambers. The product is submitted to fractionation, and separated into heavy oil, middle oil and petrol.

QUESTIONS

1. Describe the occurrence, composition, and probable origin of natural petroleum. Give an outline, in brief, of the method of treatment of the crude product and indicate the main applications of the derived materials.
(*Punjab, B.Sc., 1942*)

2. Describe briefly the modern method of "Petroleum Refining". Explain the meaning of the terms : (*a*) Octane Number, (*b*) Cracking of Oils. (*Lahore, B.Sc., 1950*)

3. Describe briefly the process of petroleum refining. What end products are obtained as a result of this process and to what uses are they put ?

Explain the meaning of the term cracking and describe its importance to the petroleum industry. (*Punjab, B.Sc., 1959*)

4. Write short notes on *any two* of the following :—

(*i*) Straight run gasoline, (*ii*) Cracked gasoline, (*iii*) knocking, (*iv*) Octane number, (*v*) Ethyl fluid, (*vi*) Isomerization. (*Lucknow, B.Sc., Prev., 1961*)

5. Name some important substances obtainable today from natural petroleum. From what *other* sources, and how, is petroleum obtainable ? What is a petrol substitute and why is it needed ? (*Banaras, B.Sc., 1947*)

6. Write short notes on any *three* of the following : (*a*) Knocking, (*b*) Octane number, (*c*) Reforming, (*d*) Aviation petrol, (*e*) Petrol substitutes. (*Lucknow, B.Sc., 1959*)

7. Write short notes on (*i*) Anti-knock compounds, (*ii*) Synthetic petrol. (*Lucknow, B.Sc., 1960*)

8. Write an eassy on petroleum and its fractional distillation. (*Allahabad, B.Sc., 1951*)

9. Write an essay on petroleum industry. (*Annamalai, B.Sc., 1951*)

10. Give an account of the chemistry of Petroleum. Describe the methods, developed for the production of Synthetic Petrol. (*Mysore, B.Sc., 1951*)

11. What are the important products of petroleum distillation and their uses ? (*Madras, B.Sc., 1953*)

12. Give a short account of the methods employed for the production of synthetic petrol. What attempts are being made in our country for its manufacture ? (*Agra, B.Sc., 1956*)

13. Write a short note on petroleum industry with special reference to the methods of obtaining synthetic petroleum. Explain the terms : (*i*) Cracking, (*ii*) Octane value, (*iii*) Antiknock. (*Nagpur, B.Sc., 1957*)

14. Write a short note on the petroleum industry. (*Aligarh, B.Sc., 1958*)

15. Write a note on petroleum. Describe one of the methods employed for preparing synthetic petrol. (*Lucknow, B.Sc., 1954*)

16. Write a full note on natural petroleum and its utilisation. (*Nagpur, B.Sc., 1954*)

17. (*a*) Describe the different theories that have been put forward on the origin of petroleum.

(*b*) Write a short note on cracking. (*Agra, B.Sc., 1956*)

18. Write an essay on natural petroleum and the various products that can be derived from it. (*Punjab, B.Sc., 1958*)

19. Write a short note on the petroleum industry. (*Aligarh, B.Sc., 1958*)

20. What is crude oil ? How is it obtained from mines and refined ? (*Marathwada, B.Sc., 1959*)

21. Write an essay on the importance of cracking in petroleum industry. (*Lahore, Pakistan, B.Sc., 1961*)

22. Write short notes on :—

(*a*) Cracking ; (*b*) Flash point ;and (*c*) Synthetic petrol. (*Saugar, B.Sc., 1962*)

CHAPTER TWELVE

HALOGEN DERIVATIVES OF HYDROCARBONS

1. The halogen derivatives of the aliphatic hydrocarbons provide the most valuable starting material for the syntheses of aliphatic compounds, and, for this reason, are dealt with before any other class of derivatives.

HALOGEN DERIVATIVES OF ALKANES

2. **Monohalogen Derivatives.**—These are derived from the paraffin hydrocarbons by the replacement of only one hydrogen atom by a halogen atom. They may also be regarded as *esters* of the halogen hydracids, and, for this reason, they are more commonly called **alkyl halides.**

3. **Preparation of Alkyl Halides.**—The following methods are available for the preparation of alkyl halides :—

(1) **Halogenation of Alkanes.** Halogen derivatives of alkanes can be obtained by thermal, photochemical or catalytic halogenation of alkanes (see page 141). The reaction is not well suited for laboratory-scale preparations, owing to the difficulty of separation of the chlorinated products into individual components. It has, however, found considerable use in the large-scale production of chlorinated hydrocarbon *mixtures* for use as solvents ; no separation into individual components being necessary here. It has also been used in special processing of suitable fractions from petroleum distillation. Thus, the C_5-cut, consisting of a mixture of *n*-pentane and isopentane, yields a mixture of chlorinated pentanes, which when hydrolysed with aqueous alkali gives a mixture of amyl alcohols called **"Pentasol".**

(2) **Addition of Halogen Hydracids to Alkenes.** Alkyl halides are obtainable from alkenes through addition of hydracids (page 157). The reaction between HCl and ethylene is carried out in the presence of such catalysts as $AlCl_3$ and $BiCl_3$, and is employed for the commercial preparation of ethyl chloride. With higher alkenes, addition of HCl or HBr is carried out in the liquid phase, and proceeds readily even in the absence of a catalyst.

(3) **From Alcohols.** The most widely used method for the preparation of alkyl halides is based on the replacement of the OH group of an alcohol by a halogen atom, using a variety of reagents, *viz.*,

halogen hydracids, phosphorus tri- and penta- chlorides and thionyl chloride.

(*i*) *By the action of a Halogen Hydracid.* Alkyl chlorides, bromides and iodides may be conveniently prepared by the action of the corresponding halogen hydracids on an alcohol.

Alkyl chlorides are best obtained by **Groves' process**, which consists in passing HCl gas into the alcohol in the presence of zinc chloride; *e.g.*,

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

The zinc chloride serves as an activator of the acid, and, by using a mixture of concentrated hydrochloric acid and zinc chloride, *n*-propyl, *n*-butyl and *sec*-butyl alcohols can be readily converted into the chlorides at 130° to 140°C in yields as high as 70 to 80 per cent.

Alkyl bromides and iodides are more readily obtained by this method than the chlorides, no zinc chloride need be added in these cases. The method employed consists in refluxing the alcohol with an excess of constant-boiling hydrobromic acid (48% HBr) or constant-boiling hydriodic acid (57% HI), a little sulphuric acid being used in the former case only.

Alkyl iodides can also be obtained in good yields by **Stone's method** (1950), which consists in heating an alcohol with KI in 95 per cent phosphoric acid.

(*ii*) *By the action of Phosphorus Halides.* Phosphorus pentachloride and the trichloride react with alcohols in accordance with the equations :—

$$ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$$
$$3ROH + PCl_3 \rightarrow 3RCl + P(OH)_3$$

The pentachloride gives variable yields depending on the alcohol; with the trichloride, the yields are poor except for the tertiary alcohols. The tribromide and the tri-iodide give good yields with primary alcohols. With secondary alcohols, the yields are low and with the tertiary still lower.

(*iii*) *By the action of Thionyl Chloride.* An excellent method for the conversion of primary and secondary alcohols into alkyl halides (due to Darzens, 1911) consists in refluxing a mixture of the alcohol, thionyl chloride and pyridine (solvent) :

$$ROH + SOCl_2 \xrightarrow{\text{pyridine}} RCl + SO_2 + HCl$$

Higher alcohols give better yields with pure thinyl chloride or its solution in benzene.

(4) **From Carboxylic Acids.** Alkyl halides can also be obtained from carboxylic acids through their silver, mercury and potassium salts. These, when decomposed with chlorine or bromine, evolve carbon

dioxide and produce an alkyl halide containing one carbon atom less than the original carboxylic acid :

$$RCOOAg + Br_2 \rightarrow RBr + AgBr + CO_2$$

The reaction is particularly useful for preparing long-chain alkyl halides from natural fatty acids. Thus, from caprylic acid (*n*-octanoic acid), we get *n*-heptyl chloride or bromide by treatment of the potassium salt with chlorine or bromine.

The reaction also affords a useful method of **stepping down carboxylic acids and alcohols.**

4. Properties of Alkyl Halides.—

Physical Properties. Only a few of the alkyl halides, *viz.*, CH_3Cl, C_2H_5Cl and CH_3Br are gases under ordinary conditions ; the majority are colourless, pleasant-smelling liquids. Those having a high molecular weight are solids *e.g.*, cetyl (hexadecyl) iodide, $C_{16}H_{33}I$. Among halides derived from a particular alcohol, the chloride has the lowest boiling point ; the bromide boils about 22° and the iodide 50° higher than the chloride. Specifically, also, the iodides are the heaviest and the chlorides the lightest. Like other esters, alkyl halides are practically insoluble in water, but they readily dissolve in alcohol, ether, carbon disulphide and other organic solvents.

Chemical Properties.

(*a*) **Non-Polar Character.** Alkyl halides differ characteristically from the metallic halides. As is well-known, the latter compounds react instantaneously with aqueous silver nitrate, yielding a precipitate of silver halide. Alkyl halides, on the other hand, being non-electrolytes, either do not react with silver nitrate or the reaction proceeds very slowly.

(*b*) **Substitution Reactions.** It must not be concluded from (*a*) that the halogen in alkyl halides is particularly firmly bound. As a matter of fact, the aliphatic halogen compounds are amongst the most reactive of all organic compounds. The halogen atom is easily removed and replaced by other atoms or groups. This property renders them of great importance in synthetic organic chemistry, as is illustrated by the following reactions :—

(1) When an alkyl halide is treated with zinc-copper couple and alcohol, or tin and hydrochloric acid, the halogen atom is replaced by *hydrogen* with the production of the corresponding alkane :—

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \longrightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(2) When heated with aqueous potash, the halogen atom is replaced by the *hydroxyl* group, with the production of an alcohol ; *e.g.*,

$$C_2H_5I + KOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KI$$

(3) When an alkyl halide is distilled with potassium hydro-

sulphide, the halogen is replaced by the $-SH$ *group* with the production of a thio-alcohol :

$$C_2H_5Br + KSH \longrightarrow \underset{\text{Ethyl thio-alcohol}}{C_2H_5SH} + KBr$$

(4) When an alkyl halide is heated with sodium or zinc, the halogen atom of one molecule gets replaced by the *alkyl* group of the other, with the production of a higher paraffin (**Wurtz' Sythesis**) ; *e.g.*,

$$2C_2H_5I + Zn \longrightarrow \underset{n\text{-Butane}}{C_2H_5.C_2H_5} + ZnI_2$$

Similarly, when an alkyl halide is heated with a halogen derivative of a benzene hydrocarbon, along with metallic sodium and dry ether, the halogen atom of the alkyl halide gets replaced by an *aryl* group, a higher homologue of a benzene hydrocarbon being thus produced (**Fittig's Reaction**) *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Bromobenzene}}{C_6H_5Br} + 2Na \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5} + NaBr + NaI$$

(5) When an alkyl halide is heated with the sodium derivative of an alcohol, the halogen atom is replaced by an *alkoxyl* group, with the production of an ether ; *e.g.*,

$$C_2H_5I + NaOCH_3 \longrightarrow \underset{\text{Methyl ethyl ether}}{C_2H_5.O.CH_3} + NaI$$

(6) Similarly, with sliver salt of a carboxylic acid, the halogen atom gets replaced by an *acyloxyl* group, an ester being thus produced ; *e.g.*,

$$\underset{\text{Silver acetate}}{CH_3COOAg} + C_2H_5I \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgI$$

(7) When heated with an alcoholic solution of ammonia in a sealed tube, the halogen atom is replaced by an *amino group* with the production of an amine : *e.g.*,

$$C_2H_5I + NH_3 \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + HI$$

(8) When heated with potassium cyanide, the halogen atom is replaced by the *cyano group* with the production of an alkyl cyanide ; *e.g.*,

$$C_2H_5I + KCN \longrightarrow \underset{\text{Ethyl cyanide}}{C_2H_5CN} + KI$$

This reaction is of great importance, for the alkyl cyanides are easily converted into *carboxylic acids* by hydrolysis with mineral acids or alkalis :

$$C_2H_5CN + 2H_2O \longrightarrow \underset{\text{Propionic acid}}{C_2H_5COOH} + NH_3$$

Moreover, the conversion of an alkyl halide into alkyl cyanide involves the introduction of an additional atom of carbon into the molecule. Hence, it affords a means of **ascending a homologous series.** Thus, methyl alcohol (a derivative of methane) may be converted into acetic acid (a derivative of ethane) by the following series of reactions :

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{P+I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{HOH} \underset{\text{Acetic acid}}{CH_3COOH}$$

(9) When heated with silver nitrite, the halogen atom is replaced by the *nitro group* with the production of a nitro-paraffin, *e.g.*,

$$C_2H_5I + AgNO_2 \longrightarrow \underset{\text{Nitro ethane}}{C_2H_5NO_2} + AgI$$

(*c*) **Other Reactions.** The many-sided reactivity of alkyl halides and their use in synthetic organic chemistry is further shown by the following reactions that they undergo :—

1. *Action of Alcoholic Potash.* When an alkyl halide is treated with a solution of potassium hydroxide (or sodium hydroxide) in dry ethyl alcohol, two competing reactions take place :—

(*i*) Alkene formation, *e.g.*,

$$\underset{\text{Ethyl bromide}}{CH_3.CH_2Br} + KOH \longrightarrow \underset{\text{Ethylene}}{H_2C{=}CH_2} + KBr + H_2O$$

(*ii*) Hydrolysis to alcohols, *e.g.*,

$$CH_3.CH_2Br + KOH \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + KBr$$

As to which of these reactions is particularly favoured, it depends mainly on the structure of alkyl halide. With *tertiary* alkyl halides, the alkene formation is the chief reaction, the other taking place only to the extent of 2 to 3 per cent. With *primary* alkyl halides, on the other hand, reaction (*ii*) predominates, the alkene formation taking place to the extent of only 1 per cent or so. In the case of *secondary* alkyl halides, the position is more or less intermediate.

2. *Grignard's Reaction.* When a dry ethereal solution of an alkyl halide is treated with dry magnesium, an *alkylmagnesium halide* is produced ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + Mg \longrightarrow \underset{\text{Ethylmagnesium iodide}}{C_2H_5MgI}$$

Alkylmagnesium halides themselves are extremely important synthesizing agents, and are employed for preparing a large number of organic compounds, under the name of **Grignard's Reagents** (see next chapter).

3. *Formation of Zinc Alkyls.* When an alkyl halide is heated with zinc filings in an atmosphere of carbon dioxide, a *zinc alkyl halide* is formed,

$$Zn + C_2H_5I \longrightarrow C_2H_5ZnI,$$

which, on distillation, gives a *zinc alkyl* :—

$$2C_2H_5ZnI \longrightarrow (C_2H_5)_2Zn + ZnI_2$$

4. *Combination with Tertiary Amines.* Alkyl halides undergo direct addition with the tertiary amines, forming quaternary ammonium salts ; *e.g.*,

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3I \longrightarrow \underset{\text{Tetramethylammonium iodide}}{(CH_3)_4NI}$$

5. **Methyl Chloride,** or **Chloromethane** CH_3Cl, is prepared by Grove's process : Methyl alcohol, to which about half its weight of zinc chloride has been added, is saturated with hydrogen chloride. The mixture is then gently warmed in a water-bath, when methyl chloride passes over :

$$CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O$$

Methyl chloride is a colourless, sweet-smelling gas, which, when cooled under pressure, condenses to a liquid boiling at −23°. Rapid evaporation of the liquid causes intense heat absorption. The gas burns with a green-edged flame.

Uses. Methyl chloride is placed on the market in the liquid form. It is largely employed :

(1) As a methylating agent[1] in the manufacture of dyes, and

(2) For the production of low temperatures.

6. **Methyl Bromide,** CH_3Br, resembles ethyl bromide in its method of preparation and properties. It boils at 4·5°.

7. **Ethyl Chloride,** C_2H_5Cl, is also prepared by Grove's process. The apparatus used is shown in Fig. 1. Ethyl chloride is a liquid boiling at 12°. The rapid evaporation of the liquid causes intense heat absorption as in the case of methyl chloride. For this reason it is employed as a local anæsthetic.

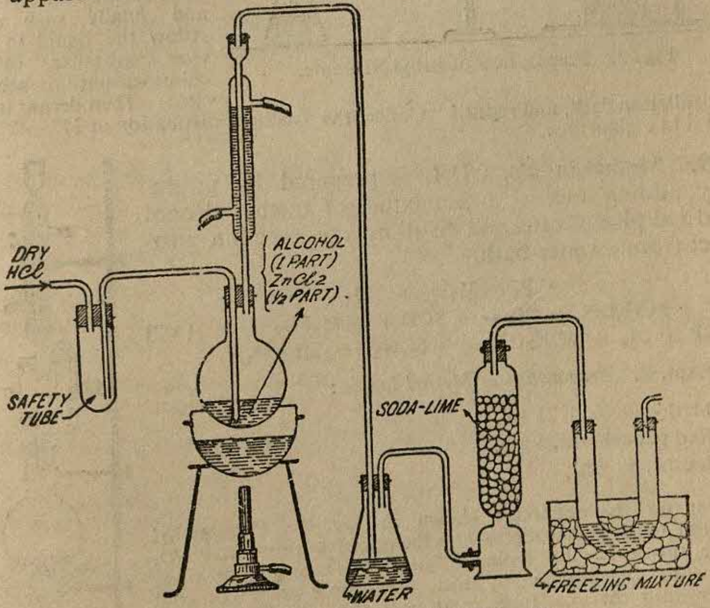


Fig. 1. Preparation of Ethyl Chloride.

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[1] *i.e.*, for introducing methyl groups in a molecule.

8. Ethyl Bromide, C_2H_5Br, is readily obtained by distilling a mixture of potassium bromide, ethyl alcohol and concentrated sulphuric acid.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$
$$C_2H_5OH + HBr \rightleftharpoons C_2H_5Br + H_2O$$

Expt. 1. Place 30 ml. of concentrated sulphuric acid in a distillation flask, add gradually 30 ml. of alcohol with constant shaking and cooling. Then add 30 gm. of coarsely powdered potassium bromide. Connect the flask to a Liebig condenser and the latter to an adapter dipping under ice cold water in a flask (Fig. 2). Heat the flask on a sand bath. Ethyl bromide passes over and collects as a heavy, oily layer at the bottom of the water in the receiver.

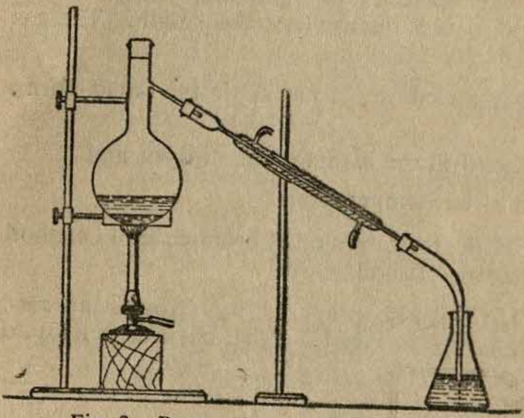


Fig. 2. Preparation of Ethyl Bromide.

Separate ethyl bromide with a tap-funnel. Wash it first with its own volume of water, then with dilute sodium carbonate solution, and finally with water. Allow the liquid to stand over granular calcium chloride, until it becomes clear. Then decant it into a distillation flask, and redistil. Collect the fraction distillation at 37°–40°, and seal it in a glass tube.

9. Methyl Iodide, CH_3I, is prepared by gradually adding iodine to a mixture of methyl alcohol and red phosphorus and distilling the reaction product from a water bath.

$$2P + 3I_2 \longrightarrow 2PI_3$$
$$\underline{3CH_3OH + PI_3 \longrightarrow 3CH_3I + H_3PO_3} \qquad [\times 2]$$
$$2P + 3I_2 + 6CH_3OH \longrightarrow 6CH_3I + 2H_3PO_3$$

Expt. 2. *Preparation of Methyl Iodide* :

Methyl alcohol, 22 ml.
Red phosphorus, 5 gm.
Iodine, 50 gm.

Fit up the apparatus shown in Fig. 3. Put methyl alcohol and red phosphorus into the round bottom flask (*R*), place the iodine on a plug of glass-wool covering the lower part of the funnel-tube (*F*), turn on a rapid stream of cold water into the condenser, and heat the water-bath. The vapour of boiling methyl alcohol rises through the side-tube (*ST*) up into the condenser the condensate continuously drops on to the iodine in *F*. and thus gradually introduces it into the flask in the form of solution. When the reaction is complete, distil the product from a water bath.

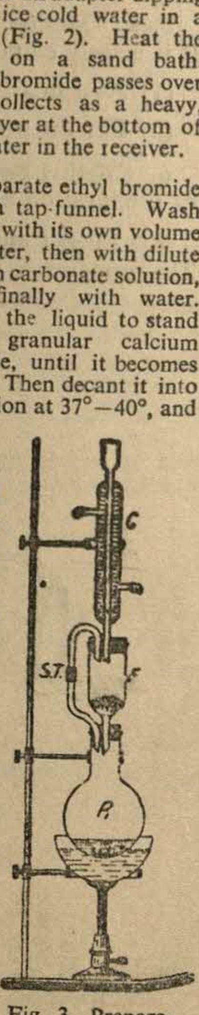


Fig 3. Preparation of Methyl iodide.

Purify methyl iodide as described under ethyl bromide.

Methyl iodide is a colourless, highly refracting liquid having a sweetish odour (b.p. 42°). On exposure to light, the liquid gradually darkens. This is due to the separation of iodine, a phenomenon common to nearly all organic compounds containing iodine.

Methyl iodide is used in the laboratory as a methylating agent in preference to methyl chloride. The ease with which it can be handled and its greater reactivity more than make up for its greater cost.

10. Ethyl Iodide, C_2H_5I, closely resembles methyl iodide, and is prepared by using ethyl alcohol instead of methyl alcohol in the above experiment. It boils at 72°. Ethyl iodide is used in synthetic organic chemistry in the same way as methyl iodide.

11. Dihalogen Derivatives.—The dihalogen derivatives of alkanes may be divided into *two groups*, according as the two halogen atoms are in union with the same or with different carbon atoms. The latter class is obtained by the direct combination of a halogen with an olefin hydrocarbon, *e.g.*,

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

while the former may be prepared either from an acetylene hydrocarbon by making it combine with two molecular proportions of a halogen hydride,

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + 2HBr \longrightarrow \underset{\text{Ethylidene bromide}}{CH_3.CHBr_2}$$

or from an aldehyde or a ketone by the action of phosphorus pentahalide.

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + PCl_5 \longrightarrow \underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} + POCl_3$$

When heated with aqueous alkalis, the derivatives containing the halogen atoms linked to two different carbon atoms, yield dihydric alcohols or glycols,

$$\underset{\text{Ethylene dibromide}}{CH_2Br.CH_2Br} + 2KOH \longrightarrow \underset{\text{Ethylene glycol}}{CH_2OH.CH_2OH} + 2KBr,$$

while the other group yields aldehydes or ketones :

$$\underset{\text{Ethylidene bromide}}{CH_3.CHBr_2} \xrightarrow{HOH} \underset{\text{(unstable)}}{CH_3CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

$$\underset{\text{2,2-Dichloropropane}}{CH_3.CCl_2.CH_3} \xrightarrow{HOH} \underset{\text{(unstable)}}{CH_3.C(OH)_2.CH_3} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

12. Dichloroethane, $C_2H_4Cl_2$, exists in two forms : (*i*) 1,2-*dichloroethane* or **ethylene dichloride**, $CH_2Cl.CH_2Cl$, and (*ii*) 1,1-*dichloro-ethane* or **ethylidene chloride**, $CH_3.CHCl_2$.

Their respective methods of preparation have already been given. The *constitution* of each compound follows from the product obtained by its hydrolysis.

13. Ethylene Dibromide, $CH_2Br.CH_2Br$, is obtained by passing ethylene into bromine. It is a colourless, pleasant-smelling liquid, boiling at 131°. It is used as a solvent and for synthetic purposes.

14. Chloroform or *Trichloromethane,* $CHCl_3$. This compound is prepared both on a commercial scale and in the laboratory by distilling alcohol or acetone with bleaching powder.

Expt. 3. 100 grams of bleaching powder is rubbed into a paste with about 400 ml. of water and placed in a two litre flask, fitted with a condenser, an adapter, and a receiver (Fig. 4). 25 ml. of alcohol or acetone is added, and the mixture gradually heated on a sand bath. If there are any signs of frothing, the flame should be temporarily removed, until the reaction moderates. The heating is continued, until no more chloroform distils over. The product is separated from the aqueous layer, shaken with dilute alkali, dried over calcium chloride and redistilled.

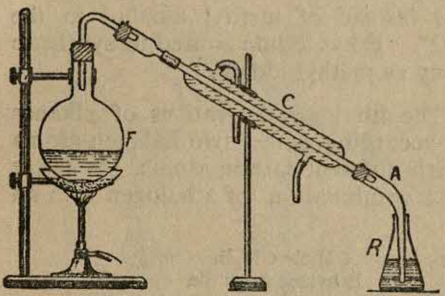


Fig. 4. Preparation of Chloroform.

The mechanism of the reaction is explained (in Sec. 17) p. 204.

Preparation of Pure Chloroform.—The chloroform prepared as above is generally impure. A convenient, though expensive, method of preparing pure chloroform consists in heating chloral or choralhydrate with a solution of caustic soda.

$$\underset{\text{Chloral}}{CCl_3.CHO} + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium formate}}{HCOONa}$$

Physical Properties.—Chloroform is a colourless liquid having a sweet, sickly odour and a sp. gr. of 1·5 at 15°. It boils at 61°, and burns with a green-edged flame. It is soluble in about 200 volumes of cold water, to which it imparts a sweet taste.

Reactions.—The more important reactions of chloroform are :—

(1) *Oxidation.*—Under the influence of air and light, chloroform is decomposed into hydrochloric acid and the highly poisonous substance carbonyl chloride or phosgene :—

$$Cl_3CH + O \longrightarrow \underset{\text{(unstable)}}{Cl_3COH} \longrightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$$

To avoid bad after-effects of carbonyl chloride, 1 per cent of pure ethyl alcohol is added to the chloroform intended for use as an anaesthetic. This reacts with the carbonyl chloride to form non-toxic, neutral ethyl carbonate :—

$$COCl_2 + 2C_2H_5OH \longrightarrow (C_2H_5)_2CO_3 + 2HCl$$

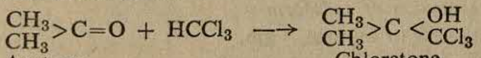
(2) *Hydrolysis.*—When heated with alcoholic potash under reflux condenser, it is hydrolysed into potassium formate and potassium chloride, which may be identified in the usual manner :

$$CHCl_3 + 4KOH \longrightarrow HCOOK + 3KCl + 2H_2O$$

(3) *Carbylamine Reaction.*—When a drop of chloroform is warmed with a drop of aniline and a few drops of alcoholic potash, a disgusting odour of phenyl isocyanide or carbylamine, is developed :

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

(4) *Condensation with Acetone.*—In the presence of alkali, chloroform undergoes condensation with acetone, yielding *trichloro-tertiary-butyl alcohol*, known as **chloretone**, which is sometimes used in medicine as a sedative and anaesthetic.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C{=}O + HCCl_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CCl_3\end{matrix}$$

Acetone Chloretone

(5) *Substitution Reactions.*—Chloroform reacts with chlorine to form carbon tetrachloride, CCl_4, with concentrated nitric acid to form **chloropicrin**, CCl_3NO_2, and with nascent hydrogen (Zn+HCl) to give methylene chloride, CH_2Cl_2.

Tests for Chloroform.—

Reactions (2) and (3) are both employed as tests for chloroform. The latter is extraordinarily sensitive and will detect 1 part of chloroform in 5,000 parts of alcohol. It is, however, not conclusive, as it is also given by bromoform, iodoform, chloral, trichloroacetic acid and other substances that yield chloroform in the presence of alkali.

In the case of reaction (2) a few drops of the product of hydrolysis are tested for the chloride radical with silver nitrate ; the remainder is then neutralized exactly, and heated with mercuric chloride solution. The formation of a precipitate of mercurous chloride and metallic mercury shows the presence of a formate.

Test for Impurities.—

Chloroform for anaesthetic purposes must be of the highest degree of purity. When shaken with water, the aqueous layer should not turn blue litmus red, nor should it give any turbidity with silver nitrate. Further, it should not turn yellow when agitated for one hour with concentrated sulphuric acid ; if the colour change occurs, it shows the presence of aldehyde, methyl alcohol, etc.

Storing of Chloroform.—To avoid oxidation, the following precautions must be observed in storing chloroform for use as an anaesthetic :—

(*a*) It is mixed with about 1 per cent of ethyl alcohol.

(*b*) The bottles must be filled almost to the stopper. This serves to exclude air.

(*c*) It is kept in the dark, or in bottles of amber colour.

Uses of Chloroform.—Chloroform is used—

(1) as an anaesthetic.

(2) as a preservative for animal or vegetable infusions or decoctions.

(3) as a flavouring agent to disguise the taste of nauseous medicines.

(4) as a non-inflammable solvent for organic substances both in the laboratory and industry.

15. Bromoform, $CHBr_3$.—Bromoform is prepared in a similar manner to chloroform by the action of bromine on alcohol or acetone.

It is a colourless, sweet liquid, soluble in alcohol, but very slightly so in water. It boils at 151°. It is used in medicine for whooping cough.

16. Iodoform, CHI_3.

Preparation. Iodoform may be prepared both in the laboratory and on the commercial scale by warming a mixture of iodine, alcohol and sodium carbonate.[1]

$$C_2H_5OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCOONa + 5NaI + 2H_2O + CO_2$$

Expt. 4. *Preparation of Iodoform—*

Ethyl alcohol or acetone, 5 gm.
Sodium carbonate crystals, 20 gm.
Iodine, 10 gm.
Water, 50 ml.

Dissolve the sodium carbonate and alcohol (or acetone) in water, and gradually add the iodine to the solution. During the addition, the temperature is gradually raised to 80°, but not higher, as iodoform is readily hydrolysed. When the deep, brown colour of iodine has disappeared, the liquid is allowed to cool and the crystals of iodoform filtered. They are then washed with a tittle distilled water, and finally purified by recrystallization from alcohol.

Manufacture. Commercially, iodoform is prepared by electrolysing an aqueous-alcoholic solution of potassium iodide and sodium carbonate. The iodine set free at the anode, acting on the alkali, produces sodium hypoiodite, which then reacts with alcohol to produce iodoform.

Physical Properties. Iodoform crystallizes in lustrous, yellow, six-sided plates, having a strong characteristic smell, and melting at 119°C. It sublimes readily, and is volatile at ordinary temperature. It is insoluble in water but soluble in alcohol and ether.

Chemical Properties. In chemical behaviour, iodoform is similar to chloroform. It gives the carbylamine reaction and is hydrolysed by caustic potash, yielding potassium iodide and potassium formate. On reduction with hydroidic acid and phosphorus, it gives methylene iodide, CH_2I_2.

Iodoform is a mild oxidizing agent (only *one* of the three iodine atoms reacting), and oxidizes arsenites, antimonites and stannites to arsenates, antimonates and stannates respectively. For example,

$$CHI_3 + Na_3AsO_3 + NaOH \rightarrow CH_2I_2 + Na_3AsO_4 + NaI$$

Use. Iodoform was formerly much employed as an antiseptic in the treatment of wounds, but it is now no longer used for this purpose because of its comparatively weak germicidal action and disagreeable odour. Its place has been taken by other more efficient antiseptics, particularly the sulpha drugs.

17. Holoform Reaction—The reaction between ethyl alcohol or acetone and an alkali hypohalite (*i.e.*, chlorine, bromine or iodine in the presence of alkali) to produce chloroform, bromoform or iodoform is a general reaction that goes under the name of **holoform reaction.** It has a definite scope, however, and is given only by those substances that have a **methyl group directly attached to the carbonyl**

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[1] The mechanism of the reaction is explained in sec. 17.

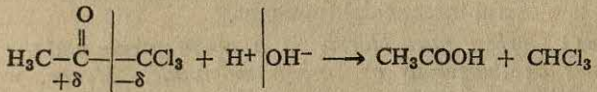
group. Thus, it is positive in the case of acetaldehyde but negative with formaldehyde or propionaldehyde. Ethyl alcohol, which produces acetaldehyde by oxidation, gives the holoform reaction, but no other primary alcohol does. All methyl ketones and those secondary alcohols that give methyl ketones on oxidation give the holoform reaction ; others do not.

Holoform reaction occurs in two distinct stages : (*i*) halogenation, and (*ii*) chain cleavage by alkali in such a way that a molecule of chloroform (bromoform or iodoform) is split off, as shown below for acetone and sodium hypochlorite :—

(*i*) $CH_3.CO.CH_3 + 3NaOCl \longrightarrow CH_3.CO.CCl_3 + 3NaOH$

(*ii*) $CH_3.CO.CCl_3 + NaOH \longrightarrow CH_3.COONa + CHCl_3$

The ease with which the cleavage of the carbon-carbon bond occurs in the holoform reaction is unusual and is ascribed to the **electrophilic character of chlorine.** This leaves a residual positive charge on the carbonyl carbon, which is thus rendered exceptionally susceptible to attack by OH⁻ ions :—



$$H_3C-\underset{+\delta}{\overset{\overset{O}{\|}}{C}}-\Big|\underset{-\delta}{-CCl_3} + H^+\Big|OH^- \longrightarrow CH_3COOH + CHCl_3$$

The signs $+\delta$ and $-\delta$ represent *fractional* positive and *fractional* negative charge acquired by the carbon atoms concerned, as the result of *electron displacement*, and are to be carefully distinguished from the *unit* positive or negative charges produced as the result of *transfer* of electrons.

Besides its use in the preparation of chloroform, bromoform and iodoform, the holoform reaction is utilized in the following directions :—

(*i*) For the detection of ethyl alcohol, secondary alcohols of the type $R.CHOH.CH_3$ and methyl ketones, the **iodoform test** being the most convenient for this purpose. A solution of iodine in potassium iodide is added to a warm solution of the substance rendered alkaline with sodium carbonate. On allowing the warm reaction mixture to stand, yellow hexagonal crystals of iodoform, having a characteristic unpleasant odour, separate out.

(*ii*) For differentiating between secondary alcohols and ketones of the type $R.CHOH.CH_3$ and $R.CO.CH_3$ from their isomers.

(*iii*) In the preparation of carboxylic acids, R.COOH, from secondary alcohols and ketones of the type mentioned above.

18. Carbon Tetrachloride, Tetrachloromethane, CCl_4. This compound is obtained on a commercial scale by the chlorination of carbon disulphide in the presence of anhydrous aluminium chloride, iron or iodine (which act as chlorine carriers) :

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

Sulphur monochloride (b. p. 138°), which is here obtained as a by-product, is separated by fractional distillation. The carbon tetrachloride fraction is further purified by shaking with caustic soda and redistillation. Carbon tetrachloride is a colourless liquid boiling at 77°.

Uses.—(1) Carbon tetrachloride readily evaporates to give a dense, incombustible vapour. For this reason, it is employed in fire extinguishers under the trade name "**pyrene**". The liquid is sprayed on to the fire, and forms a dense blanket of vapour between the burning material and air. The use of pyrene in putting out oil fires is illustrated in Expt. 5.

(2) Carbon tetrachloride is an excellent, non-inflammable solvent, and is used in the extraction of fats and oils from feeds and foodstuffs.

(3) For the same reason, it is employed in dry cleaning. When used for this purpose it may, with advantage, be mixed with petrol but only in such proportions that the mixture remains non-inflammable. Carbon tetrachloride is a very effective cleaner for bathroom tile, stoves, car parts, etc.

(4) It is a useful insecticidal fumigant.

Warning ! *Carbon tetrachloride is a* **deadly poison,** *and the vapour is four times as dangerous as carbon monoxide. Hence, when using cleaning fluids, moth sprays, etc., containing carbon tetrachloride,* **free ventilation** *must be provided. Keep the doors and the windows fully open.*

Expt. 5. Place some kerosene oil in a small dish, and set fire to it. Now pour a little carbon tetrachloride over the burning oil ; the flame is at once extinguished.

19. Acetylene Tetrachloride, Tetrachloroethane, Westron. $C_2H_2Cl_4$. This substance is prepared on a large scale by the direct combination of acetylene and chlorine. Since the combination between commercial[1] acetylene and chlorine occurs with explosive violence, it is carried out in the presence of a catalyst, when it proceeds quite smoothly. In one of the processes, a mixture of acetylene and chlorine in theoretical proportions is passed through a catalyst consisting of a mixture of iron turnings and an inert material, such as kieselguhr or broken quartz. The catalyst is placed in a steel tube cooled by a water jacket (Fig. 5). Acetylene tetrachloride is kept trickling constantly down the tube.

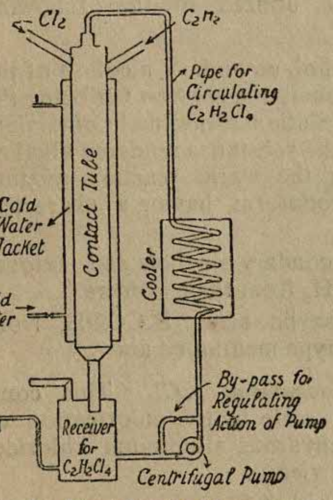

Cl_2
C_2H_2
Pipe for Circulating $C_2H_2Cl_4$
Contact Tube
Cold Water Jacket
Cooler
Cold Water
By-pass for Regulating Action of Pump
Receiver for $C_2H_2Cl_4$
Centrifugal Pump

Fig. 5. Plant for the Manufacture of Westron.

Acetylene tetrachloride is a heavy non-inflammable liquid. It is an excellent solvent for fats, oils, resins and tarry substances.

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[1] *Pure* acetylene and chlorine combine together smoothly.

Uses of Acetylene Tetrachloride.—

(1) The main use of acetylene tetrachloride is in the manufacture of *westrosol* and other chlorine compounds.

(2) It is used as a solvent for cellulose-acetate varnishes, fats and rubber.

(3) It is also used as a paint remover and a degreaser for metals, textiles and other materials.

(4) Another use of this substance is as an insecticide, *e.g.*, for white fly on tomato plants and fur-weevil in barley.

20. Fluoro Derivatives.—Fluorinated hydrocarbons cannot be prepared from alcohols by the action of hydrogen fluoride, as the position of equilibrium in this case favours hydrolysis and the use of sulphuric acid results in side reactions. The following two methods are employed :—

1. By the addition of HF to olefins ; *e.g.*,

$$CH_2{=}CH_2 + HF \xrightarrow{25^\circ,\ 10\ \text{atm.}} \underset{\substack{\text{Ethyl fluoride} \\ (\text{b.p., }-38^\circ)}}{CH_3{\cdot}CH_2F}$$

2. By the action of an organic halide with an inorganic fluoride (usually AgF, HgF_2 or CoF_3). Thus, ethyl bromide and mercuric fluoride react quantitatively at 0° to form ethyl fluoride:

$$2C_2H_5Br + HgF_2 \longrightarrow 2C_2H_5F + HgBr_2$$

21. Fluorocarbons.—The term "fluorocarbons" is applied to hydrocarbon derivatives in which *all* the hydrogen atoms have been replaced by fluorine, *e.g.*, CF_4, C_2F_6, C_3F_8, etc. The most important property of fluorocarbons is their *extreme chemical inertness.* This property was utilised during World War II in connection with the production of "atom bomb".

A general method of preparing fluorocarbons consists in passing the hydrocarbon vapour mixed with nitrogen (for dilution) over a metallic fluoride (*e.g.*, CoF_3) heated to a suitable temperature. Thus hexane, on this treatment gives **perfluorohexane** :—

$$C_6H_{14} + 28CoF_3 \xrightarrow{300^\circ} 28CoF_2 + 14HF + C_6F_{14}$$

The prefix *perfluoro* is used in naming organic compounds in which *all hydrogens linked to carbon* have been replaced by fluorine.

It is hoped that, in the near future, fluorocarbons will be produced more cheaply and put to such uses as lubricants under extreme temperature conditions and fireproofing, etc. These hopes are based on the extreme chemical indifference of these compounds, their low boiling points and low surface tension.

22. Freons. Chloro-fluoro derivatives of methane and ethane are low-boiling, non-inflammable, non-toxic and almost odourless liquids. Because of these valuable properties, they have acquired great commercial importance as **refrigerant liquids** for household refrigerators and air conditioning units. These compounds are collectively known as Freons, and the individual members are designated by various numerals. Thus, we have :—

Monofluorodichloromethane, $CHFCl_2$, Freon-21

Difluorodichloromethane, CF_2Cl_2, Freon-12

Trifluoromonochloromethane, CF_3Cl, Freon-22

Freons are also used as **insecticide propellants** in aerosol bombs (Fig. 6). A suitable insecticide (*e.g.*, DDT) is dissolved in a Freon under pressure. On opening the valve, an aerosol spray of the liquid is forced out. The freon quickly evaporates, leaving a colloidal suspension of the insecticide in the air.

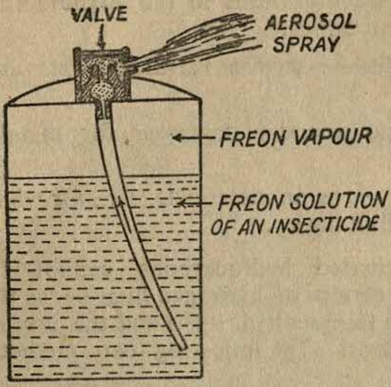


Fig. 6. Aerosol insecticide bomb.

23. Freon-12.—The first freon to be made on a commercial scale (1930) was **difluorodichloromethane**, CF_2Cl_2. It goes under the trade name Freon-12 or simply "Freon", and is now manufactured on a large scale from carbon tetrachloride by the action of hydrogen fluoride in the presence of a little antimony pentachloride (catalyst) :—

$$CCl_4 + 2HF \longrightarrow CCl_2F_2 + 2HCl$$

Freon-12 boils at $-29{\cdot}2°$, and is the most common refrigerent used in the household refrigerator (see Fig. 7). It is also used as a *propellant* in insecticide bombs.

The gas (Freon) is compressed by means of a motor driven compressor. The resulting heat is dissipated by means of a *radiator* (also called the "*condenser*") helped by a fan. Freon liquefies and the liquid moves to the cooling unit placed inside the heat-insulated chamber. Here evaporation of the liquid occurs and the requisite heat is withdrawn from the surroundings. The gas then moves outward from the expansion chamber back to the *compressor*, and the cycle is repeated again and again, until the desired low temperature has been attained. A constant-temperature device or "*thermostat*", T, is placed on the top of the cooling unit. It serves

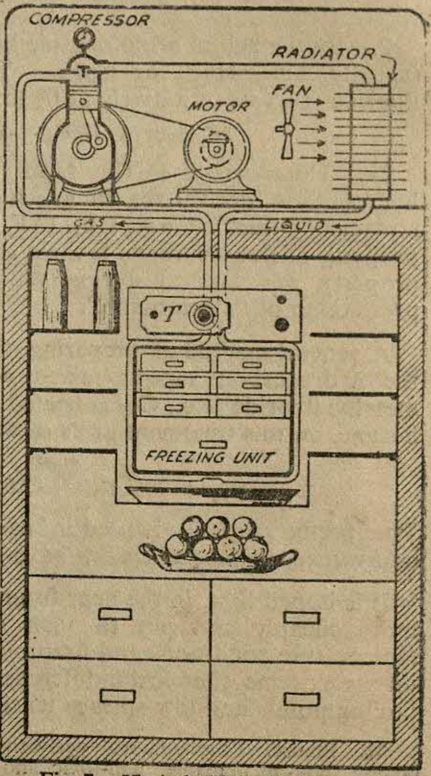


Fig. 7. Household Refrigerator.

to stop the compressor motor when the required low temperature has been reached, and starts it running again when the temperature rises above this point.

HALOGEN DERIVATIVES OF UNSATURATED HYDROCARBONS

24. General.—

Nomenclature.—The I.U.C. names of halogen derivatives of unsaturated hydrocarbons are derived from the hydrocarbon by indicating the position of the halogen atom by a numeral. If the double bond is not at the end of the chain, its position too must be indicated. The common names are derived from the alkenyl group present. The two systems of nomenclature are illustrated in the following table, which also includes the boiling points of the chlorides :

Formula	I.U.C. Name	Common Name	B.P. (°C)
$CH_2=CHCl$	Chloroethene	Vinyl chloride	−13·9
$CHCl=CHCH_3$	1-Chloropropene	Propenyl chloride	
		cis—	+32·8
		trans—	37·4
$CH_2=CCl.CH_3$	2-Chloropropene	Isopropenyl chloride	22·6
$CH_2=CHCH_2Cl$	3-Chloropropene	Allyl chloride	44·6
$CH_2CH=CHCH_2Cl$	1-Chloro-2-butene	Crotyl chloride	84
$CH\equiv CCH_2Cl$	3-Chloropropyne	Propargyl chloride	65

Classification.—The unsaturated halogen derivatives may be divided into three distinct groups having greatly different degrees of reactivity :—

(*i*) Those in which the halogen is in *direct union* with a doubly (or triply) bound carbon atom, *e.g.*, vinyl, propenyl and isopropenyl halides.

(*ii*) Those in which the halogen is attached to a singly bound carbon atom *immediately adjacent* to a doubly or triply bound carbon atom, as is the case with allyl, crotyl and propargyl halides.

(*iii*) Those in which the halogen is attached to a carbon *one or more carbon atoms removed from the* double bond ; *e.g.*,

$CH_2=CHCH_2CH_2Br$, 4-Bromobutene
$CH_2=CHCH_2CHBrCH_3$, 4-Bromopentene
$CH_2=CHCH_2CH_2CH_2Br$, 5-Bromopentene

Influence of the Double Bond on Reactivity of the Halogen Atom.—

The halogen derivatives of unsaturated hydrocarbons are expected to exhibit two characteristic features, one due to the double (or triple) bond and the other due to the halogen substituent. The presence of the double bond, however, may greatly modify the reactivity of the halogen atom. The extent of this influence depends in a remarkable manner on the *position* that the halogen atom occupies with respect to the double bond. Hence, the three classes of derivatives, indicated above, differ from one another, in a rather remarkable manner, in their relative reactivity.

(*i*) **Vinyl Type Halides.** The vinyl type of compounds, *i.e.*, those in which the halogen atom is in *direct* union with a carbon of the double bond, are **altogether indifferent to replacement reactions.** Even vinyl iodide, which is expected to be decidedly the most reactive of the three halides, does not react with aqueous alkalies and other reagents capable of replacing the halogen atom in the alkyl halide. It does not even react satisfactorily with magnesium to produce a Grignard reagent, and vinylmagnesium halides are ordinarily unavailable.[1]

(*ii*) **Allyl Type Halides.** The allyl type halides, *i.e.*, those in which the halogen is attached to a singly bound carbon atom in the immediate neighbourhood of the double bond, are extremely reactive and most readily enter into all the double decomposition reactions that the alkyl halides undergo. Indeed, these reactions occur in such compounds very much faster than in the case of alkyl halides themselves. Thus, in the double decomposition reaction with potassium iodide in acetone, which yields the corresponding iodo derivative, allyl chloride is eighty times as reactive as *n*-propyl chloride. Again, allyl iodide, when treated with sodium thiosulphate, releases its iodine 120 times as fast as *n*-propyl iodide.

Because of the high reactivity of the halogen atom in allyl halides, these compounds are of great importance in synthetic organic chemistry.

(*iii*) When the halogen atom is further removed from the double bond than in the allyl position, there is neither an activating nor a deactivating influence of the double bond on it. Such compounds undergo the usual substitution reactions at about the same rate as alkyl halides themselves.

25. Preparation.—The halogen derivatives of unsaturated hydrocarbons, unlike those of the paraffins, cannot be obtained by the direct action of halogens on the hydrocarbons, owing to the formation of addition products. They may be obtained by three different methods :

(1) *From an Unsaturated Alcohol.* When an unsaturated alcohol is treated with a halogen hydracid, or a phosphorus halide, we get the corresponding unsaturated halogen derivative : *e.g.*,

$$\underset{\text{Allyl alcohol}}{CH_2{=}CH.CH_2OH} \xrightarrow{PCl_5} \underset{\text{Allyl chloride}}{CH_2{=}CH.CH_2Cl}$$

(2) *From an Acetylene Hydrocarbon.* When an acetylene hydrocarbon is treated with *one* molecular proportion of a halogen or a halogen hydride, we get a halogen derivative of an ethylene hydrocarbon ; *e.g.*,

---

[1] However, aryl-substituted vinyl halides, *e.g.*, $(C_6H_5)_2C{=}CHBr$ and $(C_6H_5)_2C{=}C({}_6H_5)Br$, do form Grignard reagents.

$$CH{\equiv}CH \xrightarrow{+HBr} \underset{\text{Vinyl Bromide}}{CH_2{=}CHBr}$$

$$CH{\equiv}CH \xrightarrow{+Br_2} \underset{\text{1 2-Dibromo-ethylene}}{CHBr{=}CHBr}$$

(3) *From a Saturated Polyhalogen Derivative.* When a polyhalogen derivative of a saturated hydrocarbon (obtained by the direct addition of a halogen to an unsaturated hydrocarbon or by the action of PCl_5 or PBr_5 on an aldehyde or ketone) is subjected to the moderated action of alcoholic potash, a partial removal of the halogen hydride occurs with the production of an unsaturated halogen derivative ; *e.g.*,

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{+Br_2} \underset{\text{Ethylene dibromide}}{CH_2Br.CH_2Br} \xrightarrow{-HBr} \underset{\text{Vinyl bromide}}{CH_2{=}CHBr}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+Br_2} \underset{\text{Acetylene tetra-bromide}}{CHBr_2.CHBr_2} \xrightarrow{-HBr} \underset{\text{Tribromo-ethylene}}{CHBr{=}CBr_2} \xrightarrow{-HBr} \underset{\text{Dibromo-acetylene}}{CBr{\equiv}CBr}$$

$$\underset{\text{Propaldehyde}}{CH_3.CH_2.CHO} \xrightarrow{PCl_5} \underset{\text{1,1-Dichlorporopane}}{CH_3.CH_2.CHCl_2} \xrightarrow{-HCl} \underset{\text{1-Chloropropane}}{CH_3.CH{=}CHCl}$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} \xrightarrow{PCl_5} \underset{\text{2,2-Dichloropropane}}{CH_3.CCl_2.CH_3} \xrightarrow{-HCl} \underset{\text{2 Chloropropene}}{CH_3.CCl{=}CH_2}$$

Constitution.—The constitution of an unsaturated halogen derivative follows from its method of production.

26. Vinyl Halides, $CH_2{=}CHX$.

Vinyl Chloride is prepared on a large scale by the regulated addition of hydrogen chloride to acetylene, the latter being kept always in large excess.

Vinyl chloride is gaseous at ordinary temperatures. It does not react with an aqueous solution of caustic alkalis, nor with sodium ethoxide, etc. In the presence of sunlight and under the action of peroxide catalysts, it undergoes **addition polymerization,** a reaction characteristic of compounds containing the vinyl grouping, $H_2C{=}C<$, attached to an electrophylic atom or group, such as Cl, Br, CH_3COO, etc. The reaction is of great industrial importance, and is discussed under **vinyl polymers.**

Vinyl bromide is a liquid (b.p. 16°) with a pleasant, ethereal odour. It resembles vinyl chloride in general chemical behaviour, and polymerizes to a white solid, insoluble in organic solvents.

27. Allyl Halides, $CH_2{=}CHCH_2X$.—

Allyl Chloride is prepared on a commercial scale by direct substitutive chlorination of propylene (a product of petroleum cracking) at 400° to 600° :—

$$CH_2{=}CHCH_3 + Cl_2 \rightarrow CH_2{=}CHCH_2Cl + HCl$$

In the laboratory, the compound is conveniently prepared by warming allyl alcohol with hydrochloric acid :—

$$CH_2{=}CHCH_2OH + HCl \rightarrow CH_2{=}CHCH_2Cl + H_2O$$

Allyl chloride is a lachrymatory liquid (b.p. 44·6°C). Its vapour is highly inflammable and poisonous, and special precautions must be taken against these hazards.

Uses.—Allyl chloride is highly reactive, and, for that reason, is employed as an intermediate in the chemical and resin industries. The more important uses of allyl chloride are :—

(1) Allyl alcohol, which is the source of many allyl esters and their polymers, is almost entirely prepared commercially from allyl chloride.

(2) Allyl chloride is now a very important source of commercial glycerol (see chapter 21, sec. 9).

(3) Some other important chemical intermediates derived from allyl chloride are glycerol chlorohydrins, epichlorohydrins and allylamine.

(4) Pharmaceutical chemicals derived from allyl chloride include allyl isothiocyanate, allyl-substituted barbiturates (used as sedatives) and cyclopropane (an important anaesthetic).

(5) Allyl ethers of starch, got by treating starch with allyl chloride in the presence of an alkaline catalyst, play an important role in the manufacture of surface coatings, printing inks, adhesives and plastics.

Allyl Bromide is prepared on a commercial scale by bromination of propylene at 300°C and also by the interaction of allyl alcohol and hydrobromic acid. It is employed as a fumigant and as an intermediate in chemical industry.

Allyl Iodide is manufactured by the interaction of allyl chloride and sodium iodide. In the laboratory, it may be obtained from allyl alcohol, or more readily from glycerol, by the action of hydrogen iodide or iodine and phosphorus. In the case of glycerol, the reaction is supposed to occur in two stages, a tri-iodide being first formed, which then loses iodine :

$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} \xrightarrow{P+I_2} \underset{\text{Glyceryl tri-iodide}}{CH_2I.CHI.CH_2I} \xrightarrow{-2I} \underset{\text{Allyl iodide}}{CH_2{=}CH.CH_2I}$$

After drying glycerol, by previously heating the same to 280°, it is taken in a retort. The requisite amount of iodine is added and the tubulus of the retort is connected with a flask having a side tube. White phosphorus is cut into very small pieces and placed in the flask. Carbon dioxide is now passed through the side-tube of the flask, until the air in the whole of the apparatus has been completely displaced. The flask is tilted at times to gradually transfer into the retort the phosphorus pieces. The reaction ensues, and allyl iodide rapidly distils over. The distillate is collected in a well-cooled receiver and the distillation continued by heating until the contents of the retort begin to carbonize and vapours of acrolein are perceptible. The distillate is washed with dilute caustic soda solution, dried over fused calcium chloride and redistilled.

Allyl iodide is a colourless liquid (b.p. 102°) having a characteristic, mustard-like odour. It is far more reactive than alkyl halides, and readily reacts with caustic alkalis, potassium cyanide, alcoholic ammonia and dry magnesium. Allyl iodide is employed as such and as its Grignard reagent in the synthesis of olefinic compounds in general.

Allyl Chloride (b.p. 46°) and **Allyl Bromide** (b.p. 70°) are similar to allyl iodide.

28. **Propargyl Bromide,** $CH \equiv C.CH_2Br$. This is a pungent-smelling liquid obtained from propargyl alcohol by the action of PBr_5. It contains a true acetylenic function, as shown by its power to form metallic derivatives, such as $CCu \equiv C.CH_2Br$. That halogen atom is in union with a singly-linked carbon atom is shown by its capacity for double decomposition.

29. **Dichloroethylene** or **acetylene dichloride,** $CHCl = CHCl$, is obtained by the reduction of acetylene tetrachloride by means of zinc dust and water.

$$CHCl_2.CHCl_2 + Zn \longrightarrow CHCl{=}CHCl + ZnCl_2$$

Dichloroethylene is the best known solvent for rubber, and is used as a substitute for ether in fat extraction. It is possible to ignite the hot vapour, but the flame soon puts itself out.

30. **Trichloroethylene,** or **Westrosol,** $CHCl{=}CCl_2$, is obtained by heating acetylene tetrachloride with milk of lime,

$$CHCl_2.CHCl_2 \xrightarrow{-HCl} CHCl{=}CCl_2$$

The product is submitted to steam distillation, when trichloroethylene passes over.

Trichloroethylene is a heavy, non-inflammable liquid. It is employed on a very large scale as a solvent for fats, waxes, resins, rubber and other organic substances, and for dry-cleaning. Its low boiling-point and small latent heat render its recovery easy ; there is no "after smell", and delicate materials can be handled without fear of over-heating. These facts together with its non-inflammable nature account for the gradual displacement of other solvents by trichloroethylene.

QUESTIONS

1. "The aliphatic halogen compounds are amongst the most reactive of all organic compounds."

Illustrate the statement describing some of the reactions they undergo, and the uses to which they are put in synthetic organic chemistry.

2. Describe how the typical halogen derivatives of aliphatic hydrocarbons are prepared. Illustrate the importance of halogen derivatives in organic chemistry. (*Bombay, B.Sc., 1944*)

3. Discuss the synthetic uses of alkyl halides. (*Patna, B.Sc., 1958*)

4. Justify the statement : "A suitable selection of an alkyl halide can be used for synthesizing a desired aliphatic compound." (*Punjab, B.Sc., 1963*)

5. How would you prepare a pure example of ethyl bromide in the laboratory? Describe the action of the following reagents on ethyl bromide :—

(*a*) Metallic sodium ; (*b*) Zinc-copper couple ; (*c*) Aqueous potassium hydroxide ; (*d*) Potassium cyanide. (*Osmania, B.Sc., 1954*)

6. How is ethyl iodide usually prepared ? How may the iodine be detected and estimated ? By what steps may it be converted into (*a*) Ethylene and (*b*) Ethyl alcohol. (*Mysore, B.Sc., 1954*)

7. How is chloroform prepared in the laboratory ? Give equations. Describe its properties, tests and uses. (*Gauhati, B.Sc., 1954*)

8. How is chloroform prepared ? What happens when the compound is heated with (*a*) alcoholic potassium hydroxide, and (*b*) alcoholic potassium hydroxide and a primary amine ? (*Mysore, B.Sc., 1957*)

9. Describe the preparation and properties of Iodoform. (*Jammu & Kashmir, B.Sc., 1954*)

10. Show what compounds will be obtained on hydrolysing mono, di and trihalogen derivatives of ethane. Give their distinguishing tests. (*Lahore, B Sc., 1956*)

11. How are the following substances prepared (*a*) Freon, and (*b*) Westrosol. Give their uses. (*Agra, B.Sc., 1958*)

12. Give the different methods available for preparing ethyl iodide. Give its properties.

Illustrate by suitable reactions the use of ethyl iodide in organic synthesis. (*Poona, B.Sc., 1959*)

13. Describe in detail the method of preparing chloroform in the laboratory. What precautions are taken to preserve it and why ? Give a brief account of its properties and uses. (*Andhra, B.Sc., 1961*)

14. How is iodoform prepared in the laboratory ? Describe its physical and chemical properties, and state its uses.

How would you prove that iodoform contains iodine ? (*Calcutta, B.Sc., 1961*)

15. Explain with equations the preparation of Chloroform from ethyl alcohol or acetone. How does it react with (*i*) aqueous Caustic Potash and (*ii*) air in the presence of sunlight ? Why does chloroform not give a precipitate with silver nitrate ? (*Saugar, B.Sc., 1961*)

16. Give an account of the preparation and uses of alkyl halides in Synthetic Organic Chemistry. (*Annamalai, B.Sc., 1962*)

17. Describe any *six* important reactions of halogen derivatives of paraffins. Give the method of preparation, properties and uses of Allyl iodide. (*Punjab, B.Sc., 1963*)

18. Liquid *A* having vapour density 32·25 contained C=37·2, H=7·8 and Cl=55%. When heated with aqueous potash, it yielded *B* containing C=52·2, H=13·1% and no chlorine. Determine the structural formulae of *A* and *B*. What compound would be formed from *A* if alcoholic potash were used ? (*Rajasthan, B.Sc., 1951*)

Ans. (*A*) CH_3CH_2Cl (*B*) CH_3CH_2OH. The compound *A* reacting with alcoholic KOH would give ethylene, $CH_2=CH_2$.

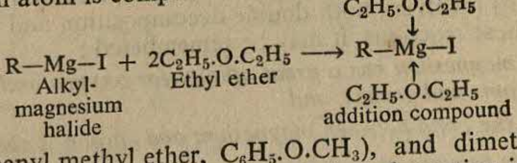
CHAPTER THIRTEEN

ORGANOMETALLIC COMPOUNDS

1. **General.**—Alkyl halides react on certain metals, yielding derivatives called organometallic compounds. The most important of the organometallic compounds are those of magnesium and zinc. The latter were discovered by Frankland in 1849, and have been of great service in the past in the synthetic organic chemistry. Their place has now been taken by **Alkylmagnesium Halides**, called the *Grignard reagents*, which are less troublesome to work with, give better yields and are of far more general utility.

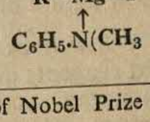
2. **Grignard Reagents**[1].—It was shown by the French chemist Grignard, in 1903, that dry magnesium in the presence of dry ether reacts with numerous organic halogen compounds, yielding **organo-magnesium halides** of the type R.Mg.Br, which remain dissolved in the ether. He also found that the organo-magnesium halides need not be isolated for synthetic purposes, since they could be used directly in ethereal solution. They are colourless solids and, unlike Frankland's reagents, are not spontaneously inflammable in air.

Though the Grignard reagent reacts as if it were simply an alkyl-magnesium halide, there is no doubt that it exists in combination with ether. In the ether molecule, there are two lone pairs of electrons on the oxygen atom, one of which is usually effective, and, in this case, is donated to the magnesium atom. The combination occurs between *two* ether molecules with a molecule of alkyl-magnesium halide. The two lone pairs of electrons from the two ether molecules are donated to the magnesium atom (which, in alkyl-magnesium halides has four valency electrons), whereby the octet of the magnesium atom is completed :



$$\underset{\substack{\text{Alkyl-}\\\text{magnesium}\\\text{halide}}}{R{-}Mg{-}I} + \underset{\text{Ethyl ether}}{2C_2H_5.O.C_2H_5} \longrightarrow \underset{\text{addition compound}}{\begin{array}{c} C_2H_5.O.C_2H_5 \\ \downarrow \\ R{-}Mg{-}I \\ \uparrow \\ C_2H_5.O.C_2H_5 \end{array}}$$

Anisole (phenyl methyl ether, $C_6H_5.O.CH_3$), and dimethylaniline, $C_6H_5.N(CH_3)_2$, may also be used in the Grignard reaction in place of ether. The co-ordination of the first compound with alkylmagnesium halide occurs through the lone pair of electrons on the oxygen atom, exactly as in diethyl ether. In the case of the latter compound, it occurs through the lone pair of electrons on the nitrogen atom, as shown in the margin.



$$\begin{array}{c} C_6H_5.N(CH_3)_2 \\ \downarrow \\ R{-}Mg{-}I \\ \uparrow \\ C_6H_5.N(CH_3 \end{array}$$

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[1] The importance of these reagents is reflected in the award of Nobel Prize for 1912 to Grignard.

3. Preparation of Grignard Reagents.—A Grignard reagent is formed with development of heat, when a halogen derivative of an aliphatic or aromatic hydrocarbon (1 mol) is added to metallic magnesium (1 gram-atom) in the presence of pure dry ether. The metal gradually disappears, and on evaporating the solution, colourless, hygroscopic crystals separate out. These consist of a Grignard reagent in combination with two molecules of ether.

For use in various syntheses, it is, however, not necessary to isolate the crystalline compound. Hence, in actual practice, an *ethereal solution* of the Grignard reagent is prepared and used as such.

Expt. 1. Preparation of Methyl Magnesium Iodide. In this preparation, the reagents used must be *thoroughly dry*. Magnesium, in the form of powder, is dried in an oven at 110°—120° for three hours. Methyl iodide is allowed to stand for some time over fused calcium chloride and then redistilled. The ether is purified by shaking several times with *small* amounts of water in order to remove alcohol, and then dried by letting it stand successively over freshly fused calcium chloride and metallic sodium.

In a clean, dry round-bottom flask of 250 ml. capacity and provided with a reflux condenser and a dropping funnel (both previously dried) place 3 grams of dry magnesium powder, and cover this with 50 ml. of dry ether. Set up the apparatus on a cold water bath, fit the upper end of the condenser with a calcium chloride tube and place in the dropping funnel a solution of 8 ml. of dry methyl iodide in dry ether. Let a few drops of the solution fall into the flask. If the reaction does not set in spontaneously within 5 minutes, a flake of iodine is added and the flask gently warmed. Once the reaction has begun, it is necessary to continue the addition of methyl iodide solution at such a rate that the reaction does not become too violent. When all the methyl iodide solution has been added the mixture is heated on the water bath, until the magnesium has completely disappeared.

4. Reactions and Synthetic Uses of Grignard Reagents.—Grignard reagents have attained a position in synthetic organic chemistry unrivalled by any other class of compounds. With the aid of these reagents, it is possible to synthesize a large variety of organic substances. The reactions of Grignard reagents may be divided into three groups : (1) double decompositions, (2) addition reactions, and (3) reactions involving both double decomposition and addition. In studying these reactions, it may be remembered :

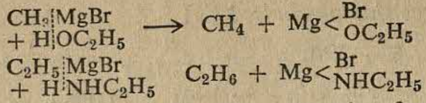
(*a*) that *magnesium has a great affinity for oxygen and other electronegative atoms and groups, and*

(*b*) that *the bond between magnesium and carbon is readily broken.*

(1) **Double decompositions.** These involve the removal of the *electropositive* group,—MgBr, of the Grignard reagent together with the *electronegative* part of the reacting molecule ; the remaining parts of the two molecules combining together to give a new product. The following are important examples of reactions of this class :—

(*i*) *Reactions with Compounds containing Active Hydrogen.* Grignard reagents undergo double decomposition with certain compounds containing active hydrogen, *e.g.*, water, alcohols, thio-alcohols, primary and secondary amines, etc., yielding *hydrocarbons.*

$$\begin{array}{l} C_2H_5 \vdots MgBr \longrightarrow C_2H_6 + Mg(OH)Br \\ +H \vdots OH \end{array}$$



$$\begin{matrix} CH_3\vdots MgBr \\ +\ H\vdots OC_2H_5 \end{matrix} \longrightarrow CH_4 + Mg{<}\begin{matrix} Br \\ OC_2H_5 \end{matrix}$$

$$\begin{matrix} C_2H_5\vdots MgBr \\ +\ H\vdots NHC_2H_5 \end{matrix} \quad C_2H_6 + Mg{<}\begin{matrix} Br \\ NHC_2H_5 \end{matrix}$$

The liberation of methane in the above reaction forms the basis of an analytical method (introduced by Zerewitinoff in 1912) for the **determination of hydroxyl groups** in a compound. A weighed amount of the substance is treated with excess methylmagnesium iodide solution, and the volume of methane set free is measured. The number of equivalents of gas evolved per mole of the compound gives the number of hydroxyl groups in the molecule.

(*ii*) *Reaction with Halogen Compounds.* Alkyl halides and acid chlorides react with Grignard reagents, yielding *hydrocarbons* and *ketones* respectively *e.g.*

$$\begin{matrix} C_6H_5\vdots MgBr \\ +\ CH_3\vdots I \end{matrix} \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + MgBrI$$

$$\begin{matrix} C_2H_5\vdots MgBr \\ +\ CH_3CO\vdots Cl \end{matrix} \longrightarrow \underset{\text{Methyl ethyl ketone}}{C_2H_5.CO.CH_3} + MgClBr$$

An excellent method of **synthesis of 1-alkenes** consists in adding allyl bromide to an ethereal solution of Grignard reagent from an alkyl halide :

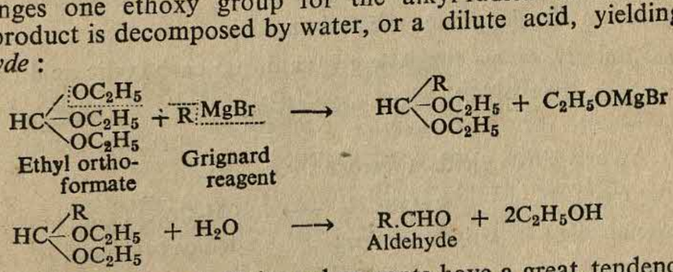
$$CH_2{=}CHCH_2Br + BrMg\,R \longrightarrow CH_2{=}CHCH_2R + MgBr_2$$

Halides of certain metals and non-metals (*e.g.*, Hg, Si, Sn, Pb, etc.,) give rise to the *alkyls* of these elements ; *e.g.*,

$$SiCl_4 + 4C_2H_5MgBr \longrightarrow \underset{\text{Silicon tetraethyl}}{Si(C_2H_5)_4} + 4MgClBr$$

$$2PbCl_2 + 4C_2H_5MgBr \longrightarrow \underset{\text{Lead tetraethyl}}{Pb(C_2H_5)_4} + Pb + 4MgClBr$$

(*iii*) *Reaction with Ethyl Orthoformate.* Ethyl orthoformate exchanges one ethoxy group for the alkyl radical of the reagent. The product is decomposed by water, or a dilute acid, yielding an *aldehyde* :

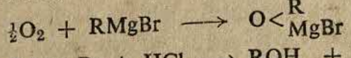


$$\underset{\text{Ethyl ortho-formate}}{HC{<}\begin{matrix} OC_2H_5 \\ OC_2H_5 \\ OC_2H_5 \end{matrix}} + \underset{\text{Grignard reagent}}{R\vdots MgBr} \longrightarrow HC{<}\begin{matrix} R \\ OC_2H_5 \\ OC_2H_5 \end{matrix} + C_2H_5OMgBr$$

$$HC{<}\begin{matrix} R \\ OC_2H_5 \\ OC_2H_5 \end{matrix} + H_2O \longrightarrow \underset{\text{Aldehyde}}{R.CHO} + 2C_2H_5OH$$

(2) **Addition Reactions.** Grignard reagents have a great tendency for directly combining with oxygen, sulphur, and compounds containing *unsaturated* groups to give addition products, which are readily decomposed by dilute hydrochloric acid, giving alcohols and other compounds :—

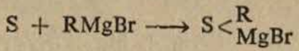
(*i*) **Oxygen** gives *alcohols* and *phenols* :



$$\tfrac{1}{2}O_2 + RMgBr \longrightarrow O{<}\begin{matrix} R \\ MgBr \end{matrix}$$

$$ROMgBr + HCl \longrightarrow \underset{\text{Alcohol}}{ROH} + MgBrCl$$

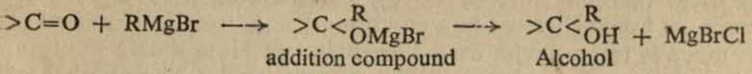
(*ii*) **Sulphur** gives *thio-alcohols*, RSH



$$\mathrm{S + RMgBr \longrightarrow S{<}^{R}_{MgBr}}$$

$$\mathrm{RSMgBr + HCl \longrightarrow RSH + MgBrCl}$$

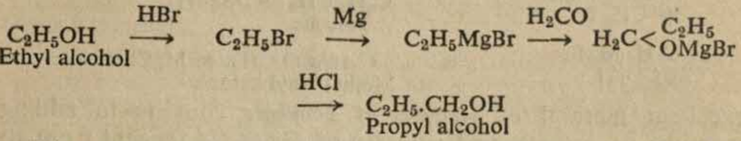
(*iii*) **Aldehydes and ketones** give *alcohols* :



$$\mathrm{{>}C{=}O + RMgBr \longrightarrow \underset{addition\ compound}{{>}C{<}^{R}_{OMgBr}} \longrightarrow \underset{Alcohol}{{>}C{<}^{R}_{OH}} + MgBrCl}$$

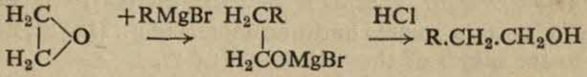
By this means, formaldehyde, $H_2C{=}O$, yields a *primary* alcohol, $R.CH_2OH$. Other aldehydes give *secondary* alcohols, R_2CHOH, while ketones give *tertiary alcohols*, R_3COH.

The reaction with formaldehyde may be used for **ascending a homologous series**, *i.e.*, preparing a higher alcohol from a lower homologue :



$$\mathrm{\underset{Ethyl\ alcohol}{C_2H_5OH} \xrightarrow{HBr} C_2H_5Br \xrightarrow{Mg} C_2H_5MgBr \xrightarrow{H_2CO} H_2C{<}^{C_2H_5}_{OMgBr} \xrightarrow{HCl} \underset{Propyl\ alcohol}{C_2H_5.CH_2OH}}$$

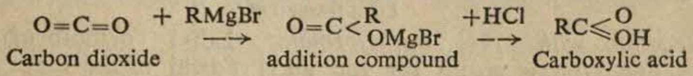
(*iv*) **Ethylene oxide** reacts like the formaldehyde, the final product being a primary alcohol :



$$\mathrm{\begin{matrix}H_2C\\ |\\ H_2C\end{matrix}{>}O \xrightarrow{+RMgBr} \begin{matrix}H_2CR\\ |\\ H_2COMgBr\end{matrix} \xrightarrow{HCl} R.CH_2.CH_2OH}$$

This reaction helps us in **ascending a series, two steps at a time.**

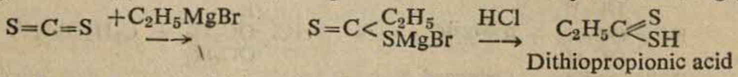
(*v*) **Carbon dioxide** gives a *carboxylic acid* :



$$\mathrm{\underset{Carbon\ dioxide}{O{=}C{=}O} \xrightarrow{+\ RMgBr} \underset{addition\ compound}{O{=}C{<}^{R}_{OMgBr}} \xrightarrow{+HCl} \underset{Carboxylic\ acid}{RC{\leqslant}^{O}_{OH}}}$$

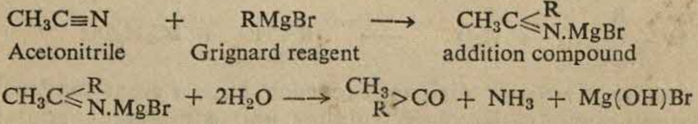
This reaction also lengthens the carbon-chain.

(*vi*) Similarly, **carbon disulphide** gives a dithio-carboxylic acid ; *e.g.*,



$$\mathrm{S{=}C{=}S \xrightarrow{+C_2H_5MgBr} S{=}C{<}^{C_2H_5}_{SMgBr} \xrightarrow{HCl} \underset{Dithiopropionic\ acid}{C_2H_5C{\leqslant}^{S}_{SH}}}$$

(*vii*) An **acid nitrile** yields a *ketone* ; *e.g.*,

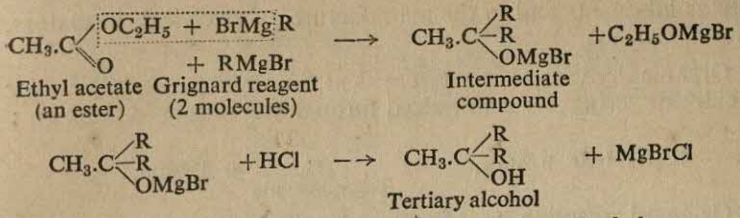


$$\mathrm{\underset{Acetonitrile}{CH_3C{\equiv}N} + \underset{Grignard\ reagent}{RMgBr} \longrightarrow \underset{addition\ compound}{CH_3C{\leqslant}^{R}_{N.MgBr}}}$$

$$\mathrm{CH_3C{\leqslant}^{R}_{N.MgBr} + 2H_2O \longrightarrow {}^{CH_3}_{R}{>}CO + NH_3 + Mg(OH)Br}$$

(3) **Reactions involving both Double Decomposition and Addition.**—In these cases, *two* molecules of the Grignard reagent are used up, one for double decomposition and the otner for addition. The following are the more important examples of such reactions :—

(*i*) **An ester** (other than formate) yields a *tertiary alcohol*, in which one of the alkyl groups is derived from the acid component of the ester and two from the Grignard reagent.



$$CH_3.C\begin{cases}\boxed{OC_2H_5 + BrMg}R\\ O\end{cases} + RMgBr \longrightarrow CH_3.C\begin{cases}R\\ R\\ OMgBr\end{cases} + C_2H_5OMgBr$$

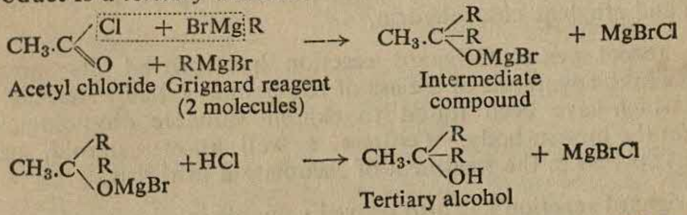
Ethyl acetate (an ester) · Grignard reagent (2 molecules) · Intermediate compound

$$CH_3.C\begin{cases}R\\ R\\ OMgBr\end{cases} + HCl \longrightarrow CH_3.C\begin{cases}R\\ R\\ OH\end{cases} + MgBrCl$$

Tertiary alcohol

Formic esters lead to the formation of *secondary alcohols.*

(*ii*) An **acid chloride** reacts in the same manner as an ester, the final product is a *tertiary alcohol* :



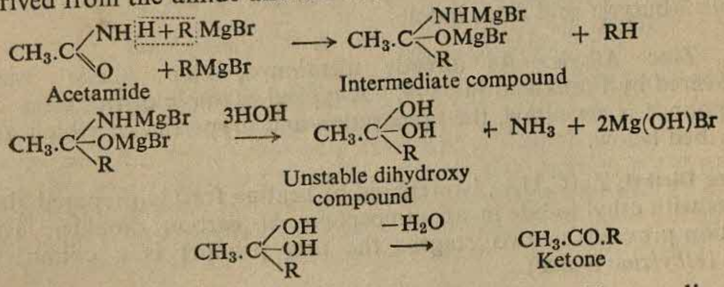
$$CH_3.C\begin{cases}\boxed{Cl + BrMg}R\\ O\end{cases} + RMgBr \longrightarrow CH_3.C\begin{cases}R\\ R\\ OMgBr\end{cases} + MgBrCl$$

Acetyl chloride · Grignard reagent (2 molecules) · Intermediate compound

$$CH_3.C\begin{cases}R\\ R\\ OMgBr\end{cases} + HCl \longrightarrow CH_3.C\begin{cases}R\\ R\\ OH\end{cases} + MgBrCl$$

Tertiary alcohol

(*iii*) An **amide** gives a *ketone* in which one of the alkyl groups is derived from the amide and the other from the Grignard reagent :



$$CH_3.C\begin{cases}NH\boxed{H+R}MgBr\\ O\end{cases} + RMgBr \longrightarrow CH_3.C\begin{cases}NHMgBr\\ OMgBr\\ R\end{cases} + RH$$

Acetamide · Intermediate compound

$$CH_3.C\begin{cases}NHMgBr\\ OMgBr\\ R\end{cases} \xrightarrow{3HOH} CH_3.C\begin{cases}OH\\ OH\\ R\end{cases} + NH_3 + 2Mg(OH)Br$$

Unstable dihydroxy compound

$$CH_3.C\begin{cases}OH\\ OH\\ R\end{cases} \xrightarrow{-H_2O} CH_3.CO.R$$

Ketone

5. Technical Applications of Grignard Reaction.—The application of the Grignard reaction in chemical industry is restricted to the production of high-priced pharmaceuticals, perfumes and silicones. The following are a few noteworthy examples :

(1) During World War II (1941-45), a large number of pure hydrocarbons, needed for petroleum research, were prepared through the Grignard reaction.

(2) The action of Grignard reagents on silicon tetrachloride, is summarized below,

$$2RMgX + SiCl_4 \longrightarrow \underset{\text{Dialkyldichlorosilane}}{R_2SiCl_2} \xrightarrow{HOH}$$

$$\underset{\text{Dialkylsilanediol}}{R_2Si(OH)_2} \xrightarrow{-H_2O} ...R_2Si-O-SiR_2-O-SiR_2...$$

leads to long-chain anhydrides as well as cyclic polymers. The resinous products thus obtained, known as **silicones**, find wide applicability as lubricants and in the manufacture of electrical insulators, silicone rubber, etc.

(3) Organic derivatives of tetracovalent tin, used as stabilizers for vinyl chloride resins, are synthesized through the Grignard reaction ; *e.g.*,

$$4C_6H_5MgBr + SnCl_4 \longrightarrow \underset{\text{Tetraphenyltin}}{(C_6H_5)_4Sn} + 4MgBrCl$$

(4) Grignard reaction is of particular interest in the field of synthetic perfumes. A simple example is that of β-phenylethyl alcohol, $C_6H_5CH_2CH_2OH$, present in otto of rose. It is manufactured, though to a small extent, by the interaction of phenylmagnesium bromide and ethylene chlorohydrin.

(5) In recent years, Grignard reaction has proved its great usefulness in the synthesis of a class of compounds called "steroids", some of which have been found to exhibit valuable physiological actions on the human body. **Cortisone**, a well known steroid, has proved its success in the treatment of rheumatoid arithritis.

(6) Grignard reaction has also proved valuable in the production of plant and animal hormones from hetrerocyclic compounds containing active hydrogen. A simple example is the production of indole-3-butyric acid from indole.

6. Zinc Alkyls.—As already mentioned, zinc alkyls were discovered by Frankland in 1849. A typical example of this class of compounds is *zinc ethyl*, the preparation and properties of which are described below.

Zinc Diethyl, $Zn(C_2H_5)_2$, is prepared by heating freshly prepared zinc filings with ethyl iodide in an atmosphere of carbon dioxide. The reaction proceeds in two stages : the first product is a colourless solid (*ethylzinc iodide*).

$$Zn + C_2H_5I \longrightarrow C_2H_5ZnI ;$$

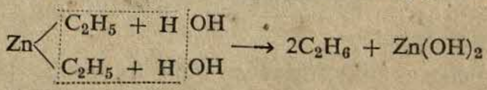
on raising the temperature, zinc diethyl is formed :

$$\begin{array}{l} C_2H_5Zn\vdots I \\ + \; C_2H_5\vdots ZnI \end{array} \longrightarrow (C_2H_5)_2Zn + ZnI_2$$

Properties. Zinc diethyl is a colourless liquid. boiling at 118°. It is spontaneously inflammable in air, and burns with a bright flame having a characteristic greenish colour, which gives off zinc oxide fumes.

The **reactions** of zinc ethyl are as follows :—

(1) It is readily decomposed by *water*, *alcohol*, and other compounds containing a hydroxyl group, *ethane* being produced :

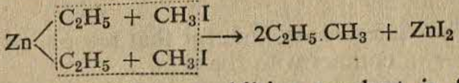


$$Zn\begin{cases} C_2H_5 + H\vdots OH \\ C_2H_5 + H\vdots OH \end{cases} \longrightarrow 2C_2H_6 + Zn(OH)_2$$

$$Zn(C_2H_5)_2 + 2CH_3OH \longrightarrow 2C_2H_6 + Zn(OCH_3)_2$$

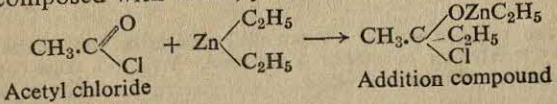
(2) It reacts with almost all *halogen compounds*, whether organic or inorganic, as illustrated by the following examples :—

(*i*) With an *alkyl halide*, a hydrocarbon is produced,

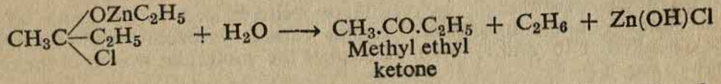


$$Zn\begin{cases} C_2H_5 + CH_3I \\ C_2H_5 + CH_3I \end{cases} \longrightarrow 2C_2H_5.CH_3 + ZnI_2$$

(*ii*) With an *acid chloride*, an additive product is formed, which when decomposed with water, yields a *ketone*; *e.g.*,

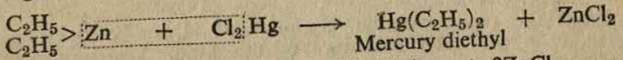


$$\underset{\text{Acetyl chloride}}{CH_3.C\begin{cases} O \\ Cl \end{cases}} + Zn\begin{cases} C_2H_5 \\ C_2H_5 \end{cases} \longrightarrow \underset{\text{Addition compound}}{CH_3.C\begin{cases} OZnC_2H_5 \\ C_2H_5 \\ Cl \end{cases}}$$



$$CH_3C\begin{cases} OZnC_2H_5 \\ C_2H_5 \\ Cl \end{cases} + H_2O \longrightarrow \underset{\substack{\text{Methyl ethyl} \\ \text{ketone}}}{CH_3.CO.C_2H_5} + C_2H_6 + Zn(OH)Cl$$

(*iii*) With chlorides of less electropositive metals and of non-metals, the ethyl group is transferred from zinc to the other element ; *e.g.*,



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}> Zn + Cl_2 Hg \longrightarrow \underset{\text{Mercury diethyl}}{Hg(C_2H_5)_2} + ZnCl_2$$

$$2Zn(C_2H_5)_2 + SiCl_4 \longrightarrow \underset{\text{Silicon tetraethyl}}{Si(C_2H_5)_4} + 2ZnCl_2$$

7. Alkylzinc Iodides.—While zinc alkyls have ceased to be of much value in synthetic organic chemistry, alkylzinc halides have retained their position to an appreciable extent They are not so violently reactive as the Grignard reagents, and, for that reason, are employed even at the present time, especially in those reactions in which the isolation of intermediate product is desired. They have been found to be particularly useful for the preparation of ketones from acid chloride ; *e.g.*,

$$CH_3.COCl + C_2H_5ZnI \longrightarrow CH_3.CO.C_2H_5 + ZnICl$$

Grignard reagents are not suitable for this purpose, as they react with the ketones produced, giving tertiary alcohols.

8. Tetraethyl Lead, $(C_2H_5)_4Pb$.—This very important organometallic compound finds considerable use as an antiknock in motor and aviation petrols. It was originally made by the Grignard reaction (sec. 2), but is now manufactured by the interaction of ethyl chloride and sodium-lead alloy :—

$$4C_2H_5Cl + 4PbNa \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$$

The resulting lead tetraethyl is separated by steam distillation.

The ethyl fluid used for leading gasoline has the following approximate composition :

Tetraethyl lead,	...	63 per cent
Ethylene dibromide,	...	26 ,,
Ethylene dichloride,	...	9 ,,
Dye	...	2 ,,

Ethylene dibromide has a definite function ; it combines with lead oxide, produced as the result of combustion of tetraethyl lead, to form volatile lead bromide, which is swept out of the engine cylinders in the exhaust gases.

Leaded gasoline is **poisonous**, and, for that reason, should never be allowed to come in contact with the skin.

QUESTIONS

1. What are organometallic compounds ? Describe the preparation and properties of a particular substance of the kind. Which of these compounds is preferred in organic synthesis and why ? (*Punjab, B.Sc., 1950*)

2. 0·1140 gm. of a thio-alcohol, RSH, on being added to an excess of an ethereal solution of ethyl magnesium bromide caused the evolution of 44·5 ml. of ethane measured at 20° and 735 mm. Calculate the molecular weight of the thio-alcohol. (*Ans.* 62)

3. 0·4328 gm. of a mixture of ethyl alcohol and ether when treated with an excess of methylmagnesium iodide gave 48·33 ml. of methane, measured at 20° and 755 mm. Calculate the percentage of alcohol in the mixture. (*Ans.* 21·2%)

4. What are organometallic compounds ? Describe the preparation and properties of a particular substance of this kind. Which of these compounds is preferred in organic synthesis and why ? (*Lahore, B.Sc., 1950*)

5. Describe in detail the preparation of Grignard reagent from methyl iodide. How could (*a*) methane, (*b*) trimethylcarbinol and (*c*) acetic acid be prepared from this reagent ? (*London, B.Sc., 1953*)

6. How would you prepare a Grignard reagent ? Describe its uses in synthetic Organic Chemistry. (*Jammu & Kashmir, B.Sc., 1954*)

7. Give the preparation and synthetic uses of Methylmagnesium Iodide. (*Mysore, B.Sc., 1953*)

8. How is methylmagnesium iodide prepared ? From it how would you prepare (*a*) isopropyl alcohol, and (*b*) tertiary butyl alcohol (*c*) acetic acid, (*d*) propane, and (*e*) ethyl alcohol ? (*Rangoon, B.Sc., 1956*)

9. How would you prepare ethylmagnesium iodide ? Give a general account of its application in organic synthesis. (*Banaras, B.Sc., 1956*)

10. How is methylmagnesium iodide prepared ? Give the importance of the compound in organic synthesis. (*Osmania, B.Sc., 1956*)

11. Describe the preparation and properties of the best known organo-metallic compound. (*Nagpur, B.Sc., 1956*)

12. How are Grignard reagents prepared ? Give an account of their use in organic synthesis. (*Travancore, B.Sc., 1954*)

13. What are Grignard reagents ? Describe the synthetic uses of these substances. (*Andhra, B.Sc., 1956*)

14. (*a*) Describe a method of preparing ethylmagnesium iodide in the laboratory. Include in your answer all essential practical details, necessary for getting a good yield.

(*b*) How does it react with (*i*) ethyl cyanide, (*ii*) primary alcohol and (*iii*) formaldehyde. (*Rajasthan, B.Sc., 1956*)

15. What are the characteristic physical and chemical properties of organo-metallic compounds ? Why do they differ from those of metallic derivatives of organic acids ? How would you synthesise ethyl mercaptan, tertiary butyl alcohol,

acetic acid and methyl ethyl ketone with the help of Grignard's reagents ? Explain the reaction involved. (*Agra, B.Sc., 1955*)

16. How is Grignard's reagent prepared ? Describe by means of equations the uses of this reagent in synthetic Organic Chemistry. (*Poona, B.Sc., 1955*)

17. Describe, indicating the necessary precautions the preparation of a Grignard reagent. Outline its synthetic application in organic chemistry. (*Gujarat, B.Sc., 1958*)

18. Discuss the importance of Grignard's reagents in synthetic chemistry. (*Karachi, B.Sc., 1958*)

19. How is a Grignard reagent prepared ? Describe the uses of this reagent for the preparation of different types of organic compounds. (*Madras, B.Sc., 1960*)

20. How would you prepare an ethereal solution of ethylmagnesium bromide ? Show how this solution may be used for the synthesis of (*a*) propionic acid, (*b*) *n*-butyl alcohol, (*c*) methyldiethyl carbinol, (*d*) propionaldehyde. (*Ceylon, B.Sc., 1960*)

21. What is a Grignard reagent ? How is it prepared ? Illustrate the use of the reagent in organic synthesis by any *five reactions*. (*Bombay. B.Sc., 1961*)

22. How is a pure sample of ethylmagnesium bromide prepared ? Explain its synthetic importance giving equations. (*Delhi, B.Sc., 1961*)

23. How is Grignard Reagent prepared ? How does it react with :

(*i*) formaldehyde ; (*ii*) acetaldehyde ; (*iii*) acetone ; and (*iv*) water. (*Aligarh, B.Sc., 1961*)

24. Outline the preparation of a solution of ethyl magnesium bromide. How will you prepare (*a*) ethane ; (*b*) propionic acid ; (*c*) methyl ethyl ketone and (*d*) isopropyl alcohol, from it ? (*Annamalai, B.Sc., 1961*)

25. Give the method of preparation and synthetic uses of Grignard reagents. Is ether essential for the preparation ? Give reasons. (*Saugar, B.Sc., 1962*)

26. Give with suitable examples, a general account of the uses of organometallic compounds for synthetic purposes. Why are magnesium compounds preferred to zinc compounds ? (*Baroda, B.Sc., 1962*)

27. Describe the preparation, structure and synthetic application of methyl magnesium iodide. (*Vallabhbhai Vidyapeeth, B.Sc., 1962*)

28. With the aid of a suitable Grignard reagent, how will you synthesise the following ? :— (*a*) Acetone (*b*) Propanol-2 ; (*c*) Propionic acid ; (*d*) tert-butyl alcohol; and (*e*) methyl ethyl ketone. (*Gorakhpur, B.Sc., 1962*)

29. How are Grignard's reagents prepared ? State how, utilising appropriate reagents and applying Grignard's reaction at one of the stages, the following conversions may be brought about :—

(*i*) Methyl alcohol to ethyl alcohol;
(*ii*) Acetone to Isobutyric acid ;
(*iii*) Acetaldehyde to Acetone ; and
(*iv*) Benzoic acid to Benzophenone. (*Punjab, B.Sc., 1962*)

30. Describe in detail the preparation of methylmagnesium iodide. How could (*a*) propane, (*b*) tertiary butyl alcohol and (*c*) acetic acid be prepared from this reagent ? (*Lucknow, B.Sc., Preliminary, 1962*)

CHAPTER FOURTEEN

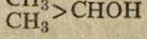
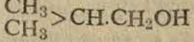
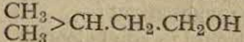
MONOHYDRIC ALCOHOLS

1. **General.**—Monohydric alcohols are derived from aliphatic hydrocarbons by the replacement of a hydrogen atom by the hydroxyl group. The most important homologous series of alcohols is that derived from alkanes and possesses the **general formula**, $C_nH_{2n+1}OH$, or $C_nH_{2n+2}O$.

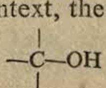
2. **Classification.**—Monohydric alcohols are divided into three classes, *primary*, *secondary* and *tertiary*, according as they contain the group $-CH_2OH$, $>CHOH$, or $\underset{\diagup}{\overset{\diagdown}{-}}COH$. The three classes are distinguished from one another by (*i*) behaviour on oxidation, (*ii*) behaviour towards hot, reduced copper, and (*iii*) behaviour of the corresponding nitroparaffins towards nitrous acid (see sec. 9).

3. **Nomenclature.**—There are three systems in use for naming alcohols :—

(1) **Alkyl Names.** This system, though of limited application, is in common use. Here, alcohols are named after the alkyl group with which the OH group is associated. Thus, we have

Methyl alcohol	CH_3OH
Ethyl alcohol	$CH_3.CH_2OH$
n-Propyl alcohol	$CH_3.CH_2.CH_2OH$
Isopropyl alcohol	 $\begin{matrix}CH_3\\CH_3\end{matrix}>CHOH$
n-Butyl alcohol	$CH_3.CH_2.CH_2.CH_2OH$
Isobutyl alcohol	 $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$
n-Amyl alcohol	$CH_3.CH_2.CH_2.CH_2CH_2OH$
Isoamyl alcohol	 $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CH_2OH$

(2) **Carbinol System.** In the carbinol system, higher homologues are regarded as derived from the first member of the series, *i.e.*, methyl alcohol. In this context, the methyl alcohol nucleus

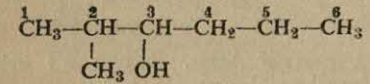


$$-\overset{|}{\underset{|}{C}}-OH$$

is termed **carbinol.** In naming alcohols only the alkyl groups linked to the carbinol nucleus are mentioned, the remaining positions being, of course, occupied by hydrogen atoms. The following examples illustrate the carbinol system :

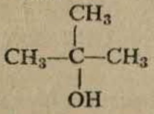
$CH_3\,CH_2OH$	Methylcarbinol
$\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}CHOH$	Methylethylcarbinol
$\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}C{<}\genfrac{}{}{0pt}{}{CH(CH_3)_2}{OH}$	Methylethylisopropylcarbinol

(3) **Geneva System.** In naming an alcohol in this system, select the *longest possible hydrocarbon chain* and use the suffix *-ol* to indicate the homologous series. The positions of the side chains and that of the OH group are indicated by numerals, using the same conventions as in the case of hydrocarbons. In naming a di- or tri-hydric alcohol the suffix *-diol* or *-triol* is employed. The following are a few illustrative examples :



$$\overset{1}{C}H_3-\underset{CH_3}{\overset{2}{C}H}-\underset{OH}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

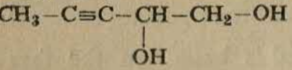
2-Methylhexanol-3



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

2-Methylpropanol-2

$CH_3-CH_2-CH=CH-CH_2-CH_2-OH$ 3-Hexeneol-1



$$CH_3-C\equiv C-\underset{OH}{CH}-CH_2-OH$$

3-Pentynediol-1,2

4. **Isomerism.**—The structural isomerism among alcohols may be due to (*i*) difference in the linking of carbon chain, (*ii*) the difference in position of the hydroxyl group in the chain, or (*iii*) both these at the same time. An alcohol which is derived from a normal hydrocarbon is termed a *normal* alcohol.

Methyl and ethyl alcohols occur only in one form. There are two propyl alcohols, one primary and the other secondary :—

(1) $CH_3.CH_2.CH_2.OH$ Normal propyl alcohol

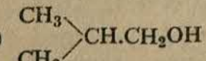
(2) $CH_3.CH(OH).CH_3$ Isopropyl alcohol

There are four butyl alcohols, two derived from normal butane (1 and 2) and two from isobutane (3 and 4) :—

(1) $CH_3.CH_2.CH_2.CH_2OH$ Normal primary butyl alcohol

(2) $CH_3.CH_2.CH(OH).CH_3$ Normal secondary butyl alcohol

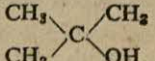
(3)



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH.CH_2OH$$

Isobutyl alcohol

(4)



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{<}\genfrac{}{}{0pt}{}{CH_3}{OH}$$

Tertiary butyl alcohol

SATURATED MONOHYDRIC ALCOHOLS

5. **Methods of Formation.**—Monohydric alcohols derived from alkanes can be obtained by the following general methods :—

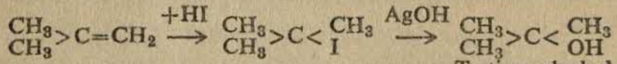
(1) **By Hydrolysis of Alkyl Halides.** When an alkyl halide is brought

into contact with silver hydroxide, or boiled with an aqueous solution of an alkali hydroxide, it is converted into an alcohol:

$$C_2H_5Br + AgOH \longrightarrow C_2H_5OH + AgBr$$

Since the alkyl halides can be obtained from alkanes by substitution, and also from the alkenes by the addition of a halogen hydracid, the aliphatic alcohols may be indirectly produced from these hydrocarbons. In the case of alkenes, the addition of the halogen hydracid always occurs in accordance with Markownikoff's rule. Hence, if we start with an alkene (other than ethylene), we get a *secondary* or a *tertiary alcohol*:

$$CH_3.CH{=}CH_2 \xrightarrow{+HI} CH_3.CHI.CH_3 \xrightarrow{AgOH} \underset{\text{Secondary alcohol}}{CH_3.CH(OH).CH_3}$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH_2 \xrightarrow{+HI} \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}CH_3\\I\end{matrix} \xrightarrow{AgOH} \underset{\text{Tertiary alcohol}}{\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}CH_3\\OH\end{matrix}}$$

(2) **By Hydrolysis of Esters of Carboxylic Acids.** When an ester is boiled with an alkali, it is hydrolysed to give an alcohol:

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + KOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + CH_3COOK$$

The method is chiefly employed for preparing certain *higher alcohols* present in ethereal oils and waxes occurring in nature. The preparation of glycerol from fats and oils is another important example.

An indirect application of this method is based on the fact that *alkyl halides*, when heated with silver acetate or potassium acetate, give rise to alkyl acetates. These latter, when boiled with alkali solutions, form alcohols:

$$C_2H_5I + CH_3COOAg \longrightarrow CH_3COOC_2H_5 + AgI$$
$$CH_3COOC_2H_5 + KOH \longrightarrow C_2H_5OH + CH_3COOK$$

This method is much used in the preparation of higher alcohols, since the higher alkyl halides (*e.g.*, hexyl chloride), on direct treatment with alkalis, give rise mainly to alkenes,

$$CH_3.(CH_2)_4.CH_2Cl + KOH \longrightarrow CH_3.(CH_2)_3.CH{=}CH_2 + KCl + H_2O,$$

the yield of alcohol being very small.

(3) **From Alkenes through Alkyl Hydrogen Sulphates.** Another application of the above method consists in dissolving an *alkene* in concentrated sulphuric acid and boiling the solution with water. Thus:

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4$$
$$C_2H_5.HSO_4 + H_2O \longrightarrow C_2H_5OH + H_2SO_4$$

(4) **By Reduction of Aldehydes and Ketones.** Aldehydes and Ketones, on treatment with reducing agents, add two atoms of hydrogen at the carbonyl group, yielding the corresponding primary and secondary alcohols:

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$
$$\underset{\text{Acetone}}{CH_3COCH_3} + 2H \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3}$$

The various methods for bringing about the reduction of aldehydes and ketones to alcohols are:—

(*i*) **Catalytic Reduction.** This is a general reaction applicable to all types of unsaturation (*i.e.*, carbonyl double bond, ethylenic linkage, etc.). It consists in shaking the compound to be reduced (if necessary, as solution in a suitable solvent) with finely divided catalyst in an atmosphere of hydrogen, usually under pressure. The catalysts commonly employed for the purpose are platinum, palladium or nickel. The most commonly used nickel catalyst at the present time is the so-called **'Raney Nickel'**. This is prepared by a method invented by Murray Raney in 1927. The method consists in treating a commercially available alloy of nickel and aluminium (about equal parts) with sodium hydroxide. The aluminium component of the alloy is dissolved out as sodium aluminate, leaving the nickel in an exceedingly fine and active form.[1]

(*ii*) **Reduction by Nascent Hydrogen.**[2] A metal undergoing chemical dissolution in acid, alkali or alcohol acts as an active reducing agent for aldehydes and ketones. Metals such as iron, tin and zinc in the presence of dilute acetic acid are generally used for the purpose. Zinc dust with alcoholic NaOH and sodium amalgam with aqueous alcohol are also employed. Sodium and alcohol provide a very efficient reducing agent for aldehydes, ketones and esters (*Bouveault-Blanc reduction*, 1903). This method is of particular importance for the reduction of esters (*see* below).

(*iii*) **Reduction by Metal Hydrides.** Darzens, in 1947, found that sodium hydride, NaH, is a better reducing agent for aldehydes, ketones and esters than sodium and alcohol as employed in Bouveault-Blanc reaction. In the same year, Nystrom and Brown reported that **lithium aluminium hydride,**[3] $LiAlH_4$, affords an *ideal reagent for the reduction of not only aldehydes and ketones but also carboxylic acids and their esters* and chlorides.

Another complex hydride employed for the reduction of carbonyl compounds is **lithium borohydride, $LiBH_4$.** Like lithium aluminium hydride, it is soluble in ether, but its *action is milder and selective*. Thus, aldehydes and ketones are readily reduced even at 0°C, while esters are reduced when the reactants are refluxed for several hours. Carboxylic acids are even more resistant. In the case of a compound containing more than one reducible groups in the molecule, the more reactive group is reduced preferentially ; *e.g.*,

$$RCOCH_2CH_2COOH \xrightarrow{LiBH_4} RCH(OH)CH_2.CH_2COOH$$

A third reducing agent belonging to the same category is **sodium borohydride,** $NaBH_4$, which is insoluble in ether but soluble in water, and in methyl alcohol, without decomposition. A solution of the reagent in either of these solvents is useful for carrying out reduction of aldehydes and ketones, but is *without action on carboxylic acids and their esters.*

---

[1] Raney nickel is pyrophoric, and is generally stored under water, alcohol or any other suitable liquid.

[2] According to modern viewpoint, the reducing action of a metal undergoing chemical dissolution is due to the donation of electrons from the metal, followed by neutralization of the resulting negative charges by protons derived from the solvent (acid, alkali or alcohol) :—

$$>C{=}O \xrightarrow{+2e^-} >\bar{C}{=}\bar{O} \xrightarrow{+2H^+} >CH{-}OH$$

[3] Lithium aluminium hydride, LiAlH, discovered by Schlesinger in 1946, is prepared by the interaction of lithium hydride and aluminium chloride,

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$$

The reagent is used in solution in dry diethyl ether.

(*iv*) **Meerwein-Ponndorf Reduction**[1] (1925-26). This is an elegant method for reducing aldehydes and ketones to alcohols. It consists in heating the carbonyl compound, in benzene or toluene solution[2], with **aluminium isopropoxide** dissolved in excess isopropyl alcohol. The reagent gets oxidized to acetone, which, being the lowest boiling component, is removed from the equilibrium mixture by slow distillation.

$$\begin{tikzcd} R_2C{=}O + [(CH_3)_2CHO]_3Al \arrow[r, leftrightarrow] & {[R_2CHO]_3Al} \arrow[d, "\text{dil } H_2SO_4"] & + \; CH_3COCH_3 \\ & R_2CHOH & \end{tikzcd}$$

Aluminium isopropoxide is a **specific reagent for the reduction of the carbonyl group.** Hence, it is of particular value for the reduction of aldehydes and ketones containing some other reducible functional group, such as the double bond or the nitro-group.

(5) **By Reduction of Carboxylic Esters.** When a carboxylic ester is submitted to reduction, it usually gets converted into *two* alcohols, one corresponding to the acid and the other to the alcohol from which the ester is derived :

$$R{-}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR'} + 4H \longrightarrow RCH_2OH + HOR'$$

The reaction, since it involves addition of hydrogen coupled with the decomposition of the ester, is often referred to as **'Hydrogenolysis'** of the ester.

Three methods are available for bringing about hydrogenolysis of carboxylic esters :—

(*i*) **Bouveault-Blanc Reduction.** This method is generally applicable to aliphatic esters.[3] It consists in refluxing the ester with metallic sodium and an alcohol (usually ethyl, butyl or amyl, depending on the refluxing temperature required[4]).

(*ii*) **Catalytic Hydrogenolysis.** A second general method of reducing carboxylic esters to alcohols is high-pressure hydrogenation (100-300 atm. of hydrogen) over a copper chromite catalyst at 200-300°C. The reaction proceeds smoothly and almost quantitatively.

(*iii*) **By Lithium Aluminium Hydride.** This very efficient reducing agent has proved very satisfactory in bringing about hydrogenolysis of carboxylic esters to alcohols.

---

[1] **Meerwein-Ponndorf reduction** is the counterpart of Oppenauer oxidation of an alcohol with an excess of acetone in the presence of aluminium *t*-butoxide (*see* chapter on Aldehydes and Ketones, sec. 2/1)

[2] **Mechanism of Meerwein-Ponndorf Reaction.** Sometimes, the equation for the reaction is so written as to indicate that it is the isopropyl alcohol that is the reductant, while aluminium isopropoxide functions as the catalyst :—

$$R_2CO + (CH_3)_2CHOH \xrightarrow{\text{Al isopropoxide}} R_2CHOH + (CH_3)_2CO$$

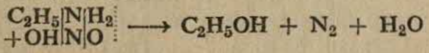
Actually, however, it appears more probable that it is the aluminium alkoxide itself that plays the role of the reducing agent, the alcohol functioning merely as the solvent. The equation for the reaction, therefore, is better written as given in the text.

[3] The method fails, however, in the case of formic esters ; on the other hand, aromatic esters get completely reduced to the hydrocarbon stage, $ArCH_3$.

[4] Esters derived from higher carboxylic acids usually require higher temperatures for hydrogenolysis.

(6) **By Reduction of Carboxylic Acids.** As compared with their esters, carboxylic acids are very resistant to reduction. The only general method by which the carboxylic acids, as such, could be reduced to primary alcohols, $RCOOH \rightarrow RCH_2OH$, is by the use of the remarkably efficient **lithium aluminium hydride** already described.

(7) **By action of Nitrous Acid on Primary Amines.** When a primary amine is treated with nitrous acid ($NaNO_2 + HCl$), the NH_2 group gets replaced by an OH group, and an alcohol is produced. Thus, ethylamine gives ethyl alcohol :



$$\begin{array}{l|l|l} C_2H_5 & N & H_2 \\ +OH & N & O \end{array} \longrightarrow C_2H_5OH + N_2 + H_2O$$

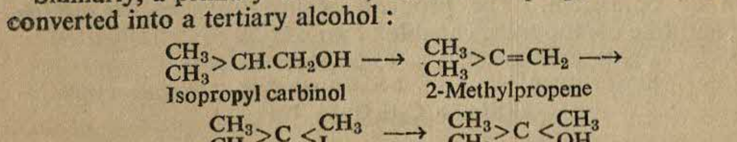
(8) **By means of Grignard's Reagents.** Grignard's reagents combine with aldehydes, ketones, ethylene oxide, esters and acid chlorides, giving addition products, which, on treatment with a dilute mineral acid, yield primary, secondary and tertiary alcohols. They also absorb oxygen and the product when decomposed with water or a dilute acid, yields an alcohol (see chap. 13, sec. 4).

(9) **By the fermentation of certain carbohydrates :** *e.g.*,

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

This method, though not very general, is of great commercial importance.

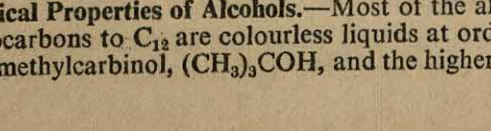
7. Conversion of Primary into Secondary and Tertiary alcohols.— This is effected through an olefine hydrocarbon, which is then made to combine with hydriodic acid, or fuming sulphuric acid. The addition occurs in accordance with Markownikoff's rule. The resulting ester is then hydrolysed, in the first case, by boiling with an aqueous solution of caustic soda, and in the second, by diluting with water and boiling. Thus, propyl alcohol may be converted into isopropyl alcohol as shown below :



$$\underset{\text{Propyl alcohol}}{CH_3.CH_2.CH_2OH} \longrightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + H_2O$$

$$CH_3.CH{=}CH_2 \xrightarrow{+H_2SO_4} \underset{\substack{\text{Isopropyl hydrogen}\\\text{sulphate}}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.HSO_4} \xrightarrow{H.OH} \underset{\text{Isopropyl alcohol}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CHOH}$$

Similarly, a primary alcohol, such as isopropyl carbinol, may be converted into a tertiary alcohol :



$$\underset{\text{Isopropyl carbinol}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.CH_2OH} \longrightarrow \underset{\text{2-Methylpropene}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>C{=}CH_2} \longrightarrow$$

$$\underset{\text{Trimethylmethyl iodide}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>C<\!\!\begin{array}{l}CH_3\\I\end{array}} \longrightarrow \underset{\text{Trimethylcarbinol}}{\begin{array}{l}CH_3\\CH_3\end{array}\!\!>C<\!\!\begin{array}{l}CH_3\\OH\end{array}}$$

8. Physical Properties of Alcohols.—Most of the alcohols derived from hydrocarbons to C_{12} are colourless liquids at ordinary temperatures. Trimethylcarbinol, $(CH_3)_3COH$, and the higher members (*e.g.*, cetyl alcohol, $C_{16}H_{33}OH$, and melissyl alcohol, $C_{30}H_{61}OH$, which occur as palmitates in spermaceti and beeswax respectively) are solids. The lower members possess a characteristic alcoholic smell and taste; the intermediate ones have an unpleasant odour ; while the higher homologues are tasteless and odourless.

In most of the organic solvents, the alcohols are miscible in all proportions. The first three members are soluble in water, but with the higher members the solubility rapidly decreases. Thus amyl alcohols are only sparingly soluble in water. The solvent power of alcohols for inorganic salts also decreases with the increasing number of carbon atoms. This will be clear from the following table, in which number of grams of each salt dissolved by 100 grams of the alcohol at 25° are given :

Salt	Water	Methanol	Ethanol	Propanol
KCl	39 9	0·53	0·022	0·004
KBr	67·7	2·17	0·142	0·035
KI	148·3	18·04	2·16	0·43

For alcohols of similar structure, the boiling point *rises* regularly with the increasing molecular weight, there being a rise of about 20° for each increment of one carbon atom. Among isomeric alcohols, the boiling-point *decreases* with a shifting of the hydroxyl group towards the centre of the chain, a shift of one step towards the centre causing a decrease of about 15°. Primary alcohols, therefore, boil at higher temperatures than the corresponding secondary alcohols, and the latter at higher temperatures than the corresponding tertiary compounds. The specific gravity increases with the rising molecular weight, but is less than one in all cases.

9. Reactions of Alcohols.—The reactions of alcohols centre round the hydroxyl group. Marked differences are exhibited depending on the number of hydrogens attached to the hydroxyl-carrying carbon atom, *i.e.*, whether the alcohol is *primary*, *secondary* or *tertiary*.

(1) **Action of Alkali Metals.** The hydrogen of the hydroxyl group is replaced when an alcohol is treated with an active metal, such as sodium or potassium. The products, called **alkoxides** are electrovalent, salt-like compounds, capable of ionization :—

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

$$C_2H_5ONa \rightleftharpoons C_2H_5O^- + Na^+$$

They are completely hydrolysed by water with regeneration of alcohols :—

$$C_2H_5ONa + H_2O \rightleftharpoons C_5H_5OH + NaOH$$

The reaction between an alcohol and an alkali metal is the fastest for methyl and ethyl alcohols, and decreases with the increasing length of the carbon chain. The structure of the latter has also a considerable influence on the rate of reaction. Thus, anhydrous *n*-butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, gives off hydrogen fairly quickly, while *tertiary* butyl alcohol, $(CH_3)_3COH$, is practically unaffected ; so much so that it may be dried with metallic sodium without appreciable loss.

(2) **Reaction with Grignard Reagents.** Alcohols react with Grignard reagents in the manner characteristic of compounds containing *active hydrogen* (chap. 13, sec. 4). The *hydrogen* of the OH group goes to the alkyl group, producing a hydrocarbon :—

$$C_2H_5O\boxed{H + CH_3}.Mg.Br \longrightarrow C_2H_5OMgBr + CH_4$$

(3) **Reaction with Carboxylic Acids—Esterification.** Alcohols react with carboxylic acids, producing *esters*, *e.g.*,

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

The net result of esterification is the removal of a molecule of water between the hydroxyl of the alcohol and the carboxyl of the carboxylic acid. The oxygen of the water produced may come either from the acid or the alcohol as shown below :—

$$CH_3CO\boxed{OH + H}OC_2H_5 \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$CH_3COO\boxed{H + HO}C_2H_5 \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

The fact is that the **oxygen of the water is derived from the carboxyl group of the acid** and *not* from the hydroxyl of the alcohol, *i.e.*, out of the two alternatives, the *first* is correct. The **most direct proof**[1] of this has been furnished by esterifying methyl alcohol containing heavy oxygen (O^{18} isotope) with a carboxylic acid. The water produced has the *normal* density. It is, therefore, clear that the oxygen component of the water comes from the carboxylic acid and not from the alcohol.

Esterification of an alcohol is catalysed by a strong acid. It is a *reversible* reaction, and so, when an ester is heated with water containing a little mineral acid, it gets *hydrolysed* to give free alcohol and the carboxylic acid.

Expt. 1. *To show the formation of an aster.* Take a few drops each of ethyl alcohol and glacial acetic acid in a test tube. Add a small quantity of concentrated sulphuric acid, and warm the mixture. A pleasant, fruity odour is developed on account of ester formation.

(4) **Action of Carboxylic Acid Anhydrides and Chlorides.** These react with alcohols in the same way as the carboxylic acids themselves, forming esters :—

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl + H}OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

$$\underset{\text{Acetic anhydride}}{CH_3CO\boxed{OCOCH_3 + H}OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

---

[1] For an indirect proof, see chap. 30, Reaction (3), *esterification of thioalcohols.*

Since the reaction of acetyl chloride with alcohols and other compounds containing an OH group is accompanied by the evolution of HCl gas, it provides a ready **test for the presence of OH group** in the molecule of a compound. The reaction is known as **acetylation.**

(5) **Reaction with Halogen Hydracids.** When an alcohol is treated with a halogen hydracid, the *hydroxyl group of the alcohol* is removed together with the hydrogen of the hydracid as water with the production of an *alkyl halide* :—

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O$$

This replacement of the OH group by a halogen atom occurs most quickly in the case of *tertiary* alcohols ; it is the slowest with primary alcohols (contrast ester formation with carboxylic acids). Thus, when *tertiary* butyl alcohol is mixed with concentrated hydrochloric acid at room temperature, there occurs a prompt separation of tertiary butyl chloride. On the other hand, *primary* butyl alcohol requires prolonged heating with hydrochloric acid in the presence of zinc chloride. The rate at which the reaction occurs with *secondary* alcohols is nearly, though not quite, as fast as with tertiary alcohols.

(6) **Reaction with Phosphorus Pentachloride.** When an alcohol is treated with phosphorus pentachloride, the *hydroxyl* of the alcohol is replaced by chlorine. Thus,

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

Like the reaction with acetyl chloride, this reaction too may be used as a **test for the hydroxyl group** in a molecule.

As with halogen hydracids, the action of phosphorus pentachloride is the fastest with tertiary alcohols and the slowest with primary alcohols.

General Rule.—In all reactions in which the *hydrogen* of the OH group of an alcohol is replaced, *primary* alcohols react most rapidly and tertiary alcohols least rapidly. On the other hand, in reactions in which the *hydroxyl* group as a whole is replaced, it is the *tertiary* alcohols that react the fastest. Secondary alcohols come in between in both cases.

(7) **Action of Concentrated Sulphuric Acid.** The action of sulphuric acid on an alcohol is two-fold : (*a*) *Esterification*, and (*b*) *Dehydration.* Hence, a variety of products can be obtained, depending on experimental conditions.

The primary action of sulphuric acid on an alcohol is the formation of an **alkyl hydrogen sulphate** :—

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \rightleftharpoons \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

This may give rise to three more products :—

(*i*) When submitted to vacuum distillation at a low temperature, it yields a **dialkyl sulphate** ; *e.g.*,

$$2C_2H_5HSO_4 \rightleftharpoons \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} + H_2SO_4$$

(*ii*) When heated with excess alcohol, an **ether** distils over. Thus, ethyl alcohol and sulphuric acid at 140° produce diethyl ether :—

$$C_2H_5HSO_4 + C_2H_5OH \xrightarrow{140^\circ} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

(*iii*) At higher temperatures, an **alkene** results ; *e.g.*,

$$C_2H_5OH \xrightarrow{165^\circ} \underset{\text{Ethene}}{C_2H_4} + H_2O$$

The *net reaction* between alcohol and concentrated sulphuric acid on heating is **dehydration of the alcohol**, which may be represented by the following two equations :—

$$C_2H_5\boxed{OH + H}OC_2H_5 \longrightarrow C_2H_5OC_2H_5 + H_2O$$

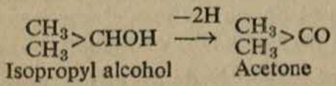
$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

These two reactions are competitive, and one or the other may be favoured, depending on the temperature and the nature of alcohol employed. With a *primary* alcohol, it is generally possible to get the ether or the alkene by selecting a suitable temperature and adjusting relative concentrations of the alcohol and the acid as exemplified above in the case of ethyl alcohol. At 140° and with excess alcohol, diethyl ether is produced; at 165° and with excess acid, ethylene is evolved. With *tertiary* alcohols, alkene formation predominates so much that it is not possible to prepare their ethers by this method.

(8) **Oxidation.** On oxidation, primary alcohols give at first aldehydes and then acids containing the *same* number of carbon atoms as the original alcohols; *e.g.*,

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{-2H} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{+O} \underset{\text{Acetic acid}}{CH_3COOH}$$

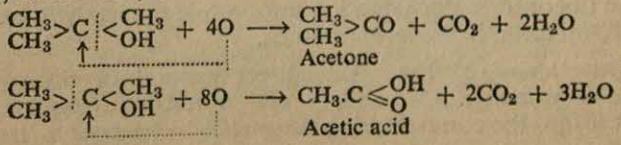
Secondary alcohols give ketones containing the *same* number of carbon atoms :



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \xrightarrow{-2H} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO$$

Isopropyl alcohol Acetone

Tertiary alcohols, since they contain no hydrogen directly linked to the hydroxyl-bearing carbon atom, do not readily undergo oxidation. On prolonged treatment with strong oxidizing agents, their molecules *break up*, yielding ketones and carboxylic acids each containing a *smaller* number of carbon atoms than the alcohol itself. Thus, trimethyl carbinol, $(CH_3)_3COH$, on vigorous oxidation, yields acetone, acetic acid, and carbonic acid :



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\begin{matrix}CH_3\\OH\end{matrix} + 4O \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + CO_2 + 2H_2O$$

Acetone

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\begin{matrix}CH_3\\OH\end{matrix} + 8O \longrightarrow CH_3.C\leqslant\begin{matrix}OH\\O\end{matrix} + 2CO_2 + 3H_2O$$

Acetic acid

In these reactions, an oxygen atom enters the molecule of a tertiary alcohol, attaching itself to the carbon atom carrying the hydroxyl group and driving out from the molecule either : (*a*) one alkyl and one hydroxyl group, or (*b*) two alkyl groups.

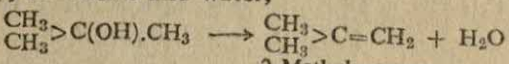
(9) **Dehydrogenation.** When the vapour of an alcohol is passed over reduced copper heated at 300°, different products are obtained, according to the nature of the alcohol. If it be primary, it yields an aldehyde and hydrogen,

$$CH_3.CH_2OH \longrightarrow CH_3.CHO + H_2$$

if secondary, a ketone and hydrogen,

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO + H_2,$$

and if tertiary, an olefine and water,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C(OH).CH_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH_2 + H_2O$$

2-Methylpropene

10. Detection of Alcohols.—The presence of an alcohol may be detected by the following tests, which must be applied *after drying the alcohol, if necessary, with an excess of anhydrous cuperic sulphate* :—

(1) Add a small piece of metallic sodium ; evolution of hydrogen.

(2) Add a small quantity of phosphorus pentachloride ; evolution of HCl gas.

(3) Add acetyl chloride or benzoyl chloride ; evolution of HCl gas and separation of an oily layer of ester.

(4) Warm with anhydrous sodium acetate and concentrated sulphuric acid ; pleasant fruity odour of an ester.

11. Distinctive Tests of Primary, Secondary and Tertiary Alcohols.—To decide whether an alcohol is primary, secondary or tertiary, the following distinctive tests my be applied :—

(1) **Oxidation or Catalytic Dehydrogenation.** The alcohol is submitted to oxidation (reaction 8) or catalytic dehydrogenation (reaction 9), and the nature of the products is investigated :—

(*i*) The formation of an aldehyde in either case proves that the alcohol is a *primary* one.

(*ii*) The formation, in either case, of a *ketone having the same number of carbon atoms in the molecule as the alcohol itself* proves the presence of a *secondary* alcohol.

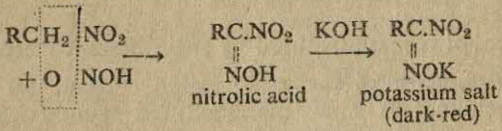
(*iii*) In the case of a *tertiary* alcohol, ketones and acids, containing a *smaller number of carbon atoms* in the molecule than in the alcohol itself are obtained in the oxidation test ; while on catalytic dehydrogenation, an olefin hydrocarbon results.

(2) **Victor Meyer's Method.** An indirect method of distinguishing between a primary, a secondary and a tertiary alcohol is first to convert it into the corresponding **nitroparaffin** by successive treatment

with HI and $AgNO_2$. The nitroparaffin is then dissolved in KOH solution, sodium nitrite is added, the solution is acidified with dilute sulphuric acid, and then again made alkaline. The production of a blood-red coloration shows it to be a primary, a blue coloration a secondary, and no coloration a tertiary alcohol.

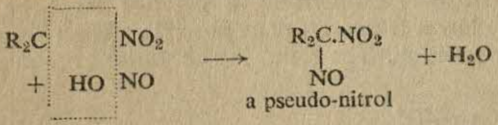
The distinction is based on the different behaviour of the corresponding nitroparaffins towards nitrous acid :

The primary nitroparaffins react with nitrous acid, yielding **nitrolic acids**, which dissolve in alkalis to give a dark-red solution :



$$\begin{array}{l} RCH_2\,NO_2 \\ +\,O\;\;NOH \end{array} \longrightarrow \underset{\text{nitrolic acid}}{\begin{array}{c} RC.NO_2 \\ \| \\ NOH \end{array}} \xrightarrow{KOH} \underset{\substack{\text{potassium salt} \\ \text{(dark-red)}}}{\begin{array}{c} RC.NO_2 \\ \| \\ NOK \end{array}}$$

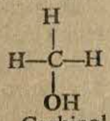
The secondary nitroparaffins react with nitrous acid, yielding blue-coloured nitro-nitroso compounds, called **pseudonitrols** :



$$\begin{array}{l} R_2C\;\;\;\;NO_2 \\ +\;\;HO\;NO \end{array} \longrightarrow \underset{\text{a pseudo-nitrol}}{\begin{array}{c} R_2C.NO_2 \\ | \\ NO \end{array}} + H_2O$$

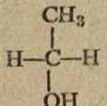
The tertiary nitroparaffins, since they contain no hydrogen directly linked to the carbon carrying the nitro group, do *not* react with nitrous acid.

(3) **Rate of Esterification.** When 1 gram-molecule each of a primary, a secondary and a tertiary alcohol is separately heated with 1 gram molecule of acetic acid under similar conditions, the rate at which esterification occurs and, therefore, the amount of the ester produced is the **greatest in the case of the primary and the least in that of the tertiary alcohol.** If we assume the rate of esterification for methyl alcohol to be 100, the rates for a few others are :



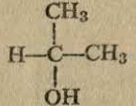
$$\begin{array}{c} H \\ | \\ H\text{—}C\text{—}H \\ | \\ OH \end{array}$$

Carbinol
100



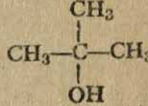
$$\begin{array}{c} CH_3 \\ | \\ H\text{—}C\text{—}H \\ | \\ OH \end{array}$$

Methyl carbinol
45·7



$$\begin{array}{c} CH_3 \\ | \\ H\text{—}C\text{—}CH_3 \\ | \\ OH \end{array}$$

Dimethyl carbinol
5·4



$$\begin{array}{c} CH_3 \\ | \\ CH_3\text{—}C\text{—}CH_3 \\ | \\ OH \end{array}$$

Trimethyl carbinol
1·4

The highest rate of esterification in the case of methyl alcohol is in accord with the fact that there is alkyl group in union with the carbon atom carrying the hydroxyl group.

(4) **Reaction with Sulphuric Acid.** When warmed with concentrated sulphuric acid, tertiary alcohols readily give olefin hydrocarbons ; primary alcohols give ethers on careful heating (though strong heating may produce alkenes also) ; secondary alcohols react rather slowly, giving both the products.

(5) **Other Reactions.** As with esterification with carboxylic acids, the

rates at which primary, secondary and tertiary alcohols react with various reagents (*e.g.*, concentrated hydrochloric acid, phosphorus pentachloride and metallic sodium) are widely different, as already described under the previous section.

12. Methyl Alcohol, *Methanol or Wood Spirit*, CH_3OH.

Occurrence. Methyl alcohol occurs in the form of methyl esters in the essential oils of many plants, *e.g.*, as methyl salicylate in oil of wintergreen, as methyl benzoate in oil of cloves, and as methyl ester of anthranilic acid in oil of jasmine and that of orange flowers.

Manufacture.—

Methyl alcohol is manufactured by two different methods :—

(1) **By Hydrogenation of Carbon Monoxide.** About 90 per cent of industrial methanol is now manufactured synthetically by the hydrogenation of carbon monoxide :

$$2H_2 + CO \rightleftharpoons CH_3OH$$

The reaction being strongly exothermic, a catalyst must be used which will work at as low a temperature as possible. High pressures, of course, favour the reaction. The following conditions are provided in the process :—

Temperature : 300° to 400°

Pressure : 200 to 300 atmospheres,

Catalyst : Chromic oxide in combination with zinc oxide.

A diagrammatic sketch of the plant used is given in Fig. 1. A mixture of water gas ($CO + H_2$) and hydrogen, after being purified from arsenic, sulphur and phosphorus compounds, is admitted into the contact chamber containing the catalyst and provided with electrically heated coils. The mixture of methanol vapour and unchanged gas passes on to a water-cooled condenser, where methyl alcohol is condensed out, while the unchanged gas is pumped back to the methanol generator.

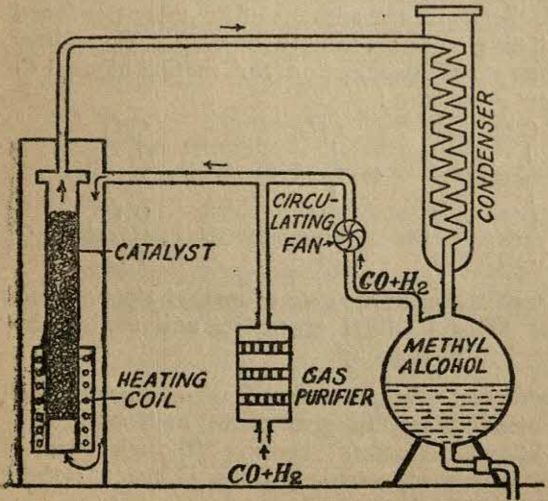


Fig. 1. Plant for manufacture of methyl alcohol by hydrogenation of carbon monoxide.

(2) **By destructive distillation of wood.** The distillation of wood is

usually carried out in large, horizontal retorts made of boiler plate (Fig. 2). The wood, after being cut into pieces of suitable size, is put into wirework cars mounted on wheels, which can be rolled in or out of the retorts as desired. The heating is effected by means of wood gas obtained during the process. As soon as the distillate begins to flow from the mouth of the condenser, the fire is turned low, as overheating causes loss of volatile matter. Towards the end, the temperature is raised quite rapidly in order to drive out the heavy tars. The products of distillation are : (*i*) **wood gas**, consisting mainly of CO, CH_4 and H_2, (*ii*) an aqueous layer known as **pyroligneous acid** which, in addition to a large proportion of water, contains acetic acid, acetone and methyl alcohol, and (*iii*) **wood-tar.** The residue consists of **charcoal**, which is removed at the end of the operation when still hot, thus saving the heat of the brickwork for the next charge.

The pyroligneous acid, which forms the upper layer, is run off from the wood-tar, and distilled. The vapours are passed through hot milk of lime, which retains acetic acid as calcium acetate, while the methyl alcohol, acetone and water pass on.

The distillate, after being dehydrated with quicklime, is fractionated to obtain crude acetone (b.p. 56°) and crude methyl alcohol (b.p. 65°).

The **crude methyl alcohol**, obtained as above, is diluted with water in order to throw out of solution the oily impurities, which collect at the surface and are run off. The aqueous layer, which still contains acetone and other impurities, is mixed with powdered anhydrous calcium chloride, whereby a crystalline compound of the composition $CaCl_2.4CH_3OH$ separates out. This is gently heated to drive off acetone and is then decomposed by distillation with water. The distillate is finally dehydrated by repeated treatment with quicklime, and is then redistilled. The product thus obtained still contains traces of acetone and other impurities.

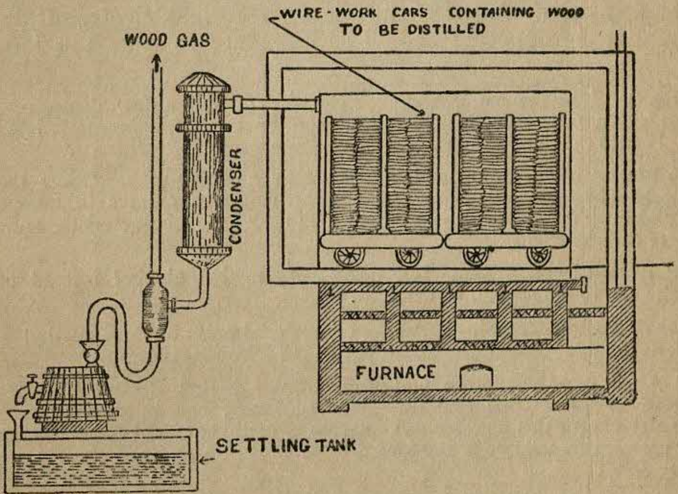


Fig. 2. Plant for the Distillation of Wood.

Purification. Pure methyl alcohol is best obtained from the commercial product by heating it with anhydrous oxalic acid (prepared by heating oxalic acid crystals at 100°). On allowing the liquid to cool, **dimethyl oxalate** separates out as crystals. These are well drained on a filter-pump, washed with a little water, and then hydrolysed with caustic soda. The methyl alcohol, thus set free, is distilled off, and is dehydrated by distillation first over quick-lime and then over metallic calcium.

Expt. 2. *To illustrate the process of destructive distillation of wood.* Fit up the apparatus shown in Fig. 3. Heat some saw-dust in the test-tube. Notice that the distillate consists of (*i*) an upper layer of pyroligneous acid, and (*ii*) a lower layer of wood-tar. Show that the gas escaping at the upper end of the tube is combustible.

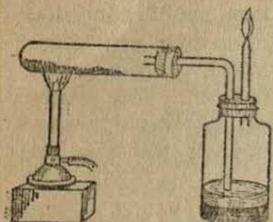


Fig. 3. Apparatus to illustrate the process of wood distillation.

Properties. Pure methyl alcohol is a colourless liquid, which boils at 65°. It possesses an agreeable, wine-like odour and a burning taste, but is poisonous. Many cases of blindness or death have been caused by drinking mixtures containing methyl alcohol. Blindness may also result from prolonged exposure to its vapour. Methyl alcohol burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air. It is miscible with water in all proportions.

Constitution. (See chap. 5, sec. 12).

Detection. The presence of methyl alcohol can be readily detected by the formation of methyl salicylate or formaldehyde. It may be differentiated from ethyl alcohol by its failure to give the iodoform test.

Expt. 3. *Identification of Methyl Alcohol.* (*i*) Boil a few drops of methyl alcohol with a little salicylic acid and a drop or two of concentrated sulphuric acid. Notice the characteristic fragrant odour of oil of wintergreen.

(*ii*) Place a few drops of methyl alcohol in a boiling-tube. Cover the same with some asbestos wool. Now heat a copper gauze to redness in an oxidizing flame and drop it immediately into the tube ; notice the characteristic suffocating odour of formaldehyde.

(*iii*) Repeat Expt. 4 (sec. 14), using *pure* methyl alcohol instead of ethyl alcohol. No iodoform can be detected.

Uses of Methyl Alcohol. From the commercial point of view, methyl alcohol is of considerable importance, and is put to the following uses :—

(1) About one-third of the total production of methyl alcohol is used as an antifreeze for automobile and aeroplane radiators, and is gradually replacing ethylene glycol for this purpose. A mixture of methyl alcohol and water containing 37 per cent by volume of the former will protect radiators against freezing, down to 30°C.

(2) Another one-third of the annual production is employed in the **manufacture of formaldehyde.**

(3) On account of its highly poisonous nature, methyl alcohol is employed as a **denaturant of ethyl alcohol** (*i.e.*, for rendering the latter unfit for human consumption as an intoxicant).

(4) Methyl alcohol, being an excellent solvent for shellac and gums is used in **the manufacture of varnish.**

(5) Methyl alcohol is the only single solvent that dissolves cellulose nitrate. For this reason, it finds important application in the **manufacture of celluloid, guncotton, spray paints** for motor and aeroplane bodies, and other nitrocellulose products.

(6) Methyl alcohol is an important **methylating agent**, and is employed in the manufacture of methylaniline, dimethylaniline, methyl chloride, dimethyl sulphate, etc

13. Ethyl Alcohol, *Ethanol*, $CH_3.CH_2OH$.—

Occurrence.—Ethyl alcohol is present in wines. It occurs naturally in the form of its esters with organic acids in many essential oils and fruits.

Syntheses.—Ethyl alcohol may be obtained by reactions analogous to those used in the case of methyl alcohol, namely :

(1) Hydrolysis of ethyl bromide or (iodide):

$$C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$$

(2) Hydrolysis of ethyl acetate :

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(3) Reduction of acetaldehyde :

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H \rightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

Three Sources of Commercial Ethyl Alcohol. Ethyl alcohol is manufactured on a large scale from three different sources :

(*i*) Saccharine materials, *e.g.*, molasses from the manufacture of cane-sugar.

(*ii*) Starchy substances, such as potatoes, barley, corn and rice.

(*iii*) Ethylene obtained from petroleum by cracking.

Three Steps in the Manufacture of Ethyl Alcohol from Sugar or Starch— The production of pure alcohol or *rectified spirit from the first two sources* consists of three main steps : (*i*) *Fermentation*, (*ii*) *Distillation* and (*iii*) *Rectification.*

First Step : Fermentation.—The sugar can be directly subjected to alcoholic fermentation, but starch must first be converted into a sugar called *maltose.*

(*a*) **Production from Sugar.** In the case of saccharine materials, fermentation is directly effected by means of yeast (*Saccharomyces*). The sugar is generally employed in the form of "**molasses**"—a dark-coloured, syrupy liquid obtained in the manufacture of cane-sugar, from which sugar cannot be profitably extracted. Molasses is diluted with water, yeast is then added, and the mixture is placed in a warm room. The liquid soon begins to ferment and effervesce, owing to slow evolution of carbon dioxide. In about 35 to 40 hours, the action is complete, when yeast is filtered off, and the fermented liquor, technically known as the "wash", is subjected to distillation.

The reactions taking place during the alcoholic fermentation of sugar have already been explained (p. 128).

(*b*) **Production from Starch.** The production of alcohol from starch consists of two distinct steps : (*i*) conversion of starch into **maltose** (*saccharification*), and (*ii*) alcoholic fermentation.

(*i*) **Saccharification.** The conversion of starch into maltose is brought about by means of an enzyme, called **diastase**, which is produced during the germination of corn, and is also found in saliva and the pancreatic juice. The diastase is not used as such, but is employed together with the whole corn in the form of **malt**, which is most conveniently obtained by the germination of barley. Barley is malted by allowing it to germinate in the dark at 15°, in layers about 5 inches thick. The germination is then stopped by raising the temperature, and the malt is crushed and extracted with water. The resulting liquid, known as **malt-extract**, contains diastase in solution.

Potatoes, rice, maize, or unmalted barley are employed as the usual source of starch. They are rasped, or crushed, and then gelatinized by treatment with super heatedsteam. The resulting mass is mixed with water, and some ground malt or malt-extract is added. The temperature is maintained at 60° to 62°C, until the conversion of starch into maltose is practically complete (about 20 minutes). The liquid is then boiled, in order to stop the action of diastase. The conversion of starch into maltose, which is a hydrolytic action, is represented by the following equation :

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_x} + xH_2O \rightarrow \underset{\text{Maltose}}{xC_{12}H_{22}O_{11}}$$

The process is known as **mashing** and the product as *mash* or *wort*.

As an alternative, starch is converted into sugar (glucose) by means of hot, dilute sulphuric acid or hydrochloric acid :

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_x} + xH_2O \rightarrow \underset{\text{Glucose}}{xC_6H_{12}O_6}$$

(*ii*) **Alcoholic Fermentation.** The saccharine liquid, obtained by either of the processes described above, is fermented by means of *yeast* at a temperature not exceeding 33°C. The fermentation takes three to four days for completion. In the case of "mash" the maltose present is first decomposed into glucose by the enzyme **maltase** present in the yeast :

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

The glucose formed is at once decomposed by **zymase**—another enzyme present in yeast, giving alcohol :

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

During fermentation, the frothing of the liquid occurs, owing to the evolution of carbon dioxide.

In case the starch has been saccharified by means of dilute sulphuric acid, or hydrochloric acid, the glucose present is directly attacked by zymase, producing alcohol.

Second Step: Distillation. The fermented liquid, which contains not more than 18 per cent of alcohol, is subjected to fractional distillation. This, in modern plants, is effected in one step and is a continuous process.

The fractionation is usually carried out in the **Coffey-still** (Fig. 4), which consists of a combination in series of two fractionating columns, known as the **analyser** and the **rectifier.** The "analyser" (shown on the left) is divided into a series of chambers by horizontal plates, *P*, perforated with holes and furnished with valves, *V*, opening upwards. From each of these an overflow pipe, *F*, passes down and dips into a shallow cup, *C*, on the next lower plate. The lower half of the "rectifier" is also divided into chambers by perforated plates, and is provided by overflow pipes.

The Coffey still works on the **counter current principle.** The liquid to be distilled passes downwards through the coils of pipe in the rectifier, where it gets heated (by steam and alcohol vapour) nearly to its boiling point, and, is then discharged at the top of the analyser. Free steam from a boiler is admitted at the base of the analyser, and, passing upward through the thin layer of liquid on the perforated plates, carries with it the vapour of alcohol and other volatile substances present in the fermented liquid.

The vapour of alcohol etc. passes out of the analyser at the top

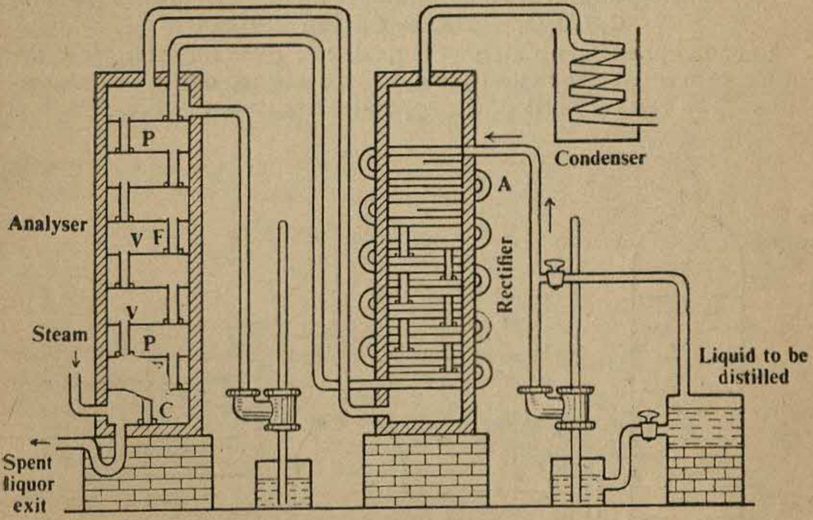


Fig. 4. Coffey Still.

and then enters the rectifier at its base. The alcohol vapour passes out at the top of the rectifier, and is conveyed to the **condenser.** The water condensed in the rectifier contains some alcohol, and is, therefore, conveyed to the top of the analyser, where it mixes with the fermented liquid. The spent liquor, entirely deprived of its volatile constituents, is drawn off at the base of the analyser.

Third Step : Rectification. When required for internal use, *e.g.*, for the preparation of spirits, liqueurs, pharmaceutical tinctures, etc., the raw spirit must be freed as much as possible from the oily mixture of higher alcohols known as **fusel oil**, which the raw spirit always contains, as well as from the low-boiling impurities, such as acetaldehyde. Formerly, fusel oil was removed from the crude spirit by dilution with water and filtration through charcoal, but at the present time fractional distillation is relied upon. The crude spirit is submitted to very careful fractional distillation in specially designed stills, and the following fractions are collected separately:

(1) *First runnings, i.e.,* low-boiling by-products consisting chiefly of acetaldehyde.

(2) *Rectified spirit*, consisting of pure aqueous alcohol containing up to a maximum of 95·5 per cent of ethyl alcohol.

(3) *Last runnings*, which consist of "fusel oil."

14. Ethyl Alcohol from Ethylene.—Very large quantities of ethyl alcohol are now manufactured from ethylene obtained by the cracking of petroleum and natural gas. The method consists of :

(1) Absorption of ethylene in cold, concentrated sulphuric acid, when ethyl hydrogen sulphate is produced,

$$C_2H_4 + H_2SO_4 \rightleftharpoons C_2H_5HSO_4$$

(2) Hydrolysing the ester by dilution with water followed by boiling,

$$C_2H_5HSO_4 + H_2O \rightleftharpoons C_2H_5OH + H_2SO_4.$$

In actual practice, no attempt is made to isolate the ester, and the absorption of ethylene and hydrolysis are carried out in one operation. The various parts of the apparatus are shown in Fig. 5.

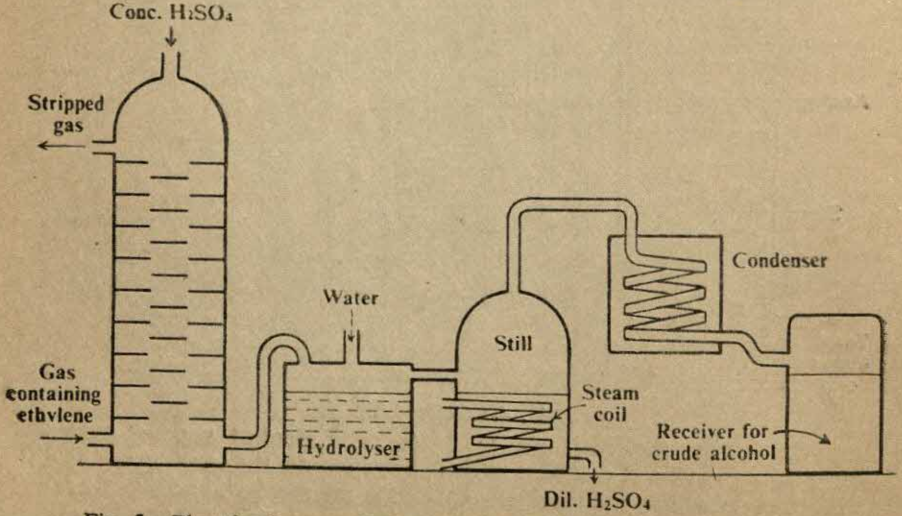


Fig. 5. Plant for the manufacture of ethyl alcohol from ethylene.

15. Absolute alcohol.—By this term is meant alcohol entirely free from water. Alcohol forms with water a constant-boiling mixture (containing 95·5 per cent of C_2H_5OH). Hence, it is not possible to effect a complete separation of the two liquids by fractional distillation. Other means must, therefore, be adopted. In the laboratory, the dehydration is effected by distillation over quicklime. The last traces of moisture (about 0·5 per cent) are then removed by treatment with a calculated amount of metallic sodium followed by redistillation.

Absolute alcohol, which, a few years back, was hardly known outside the laboratory, is now used as a solvent on a commercial scale. The removal of 4·5 per cent of water greatly increases the solvent power of alcohol for many substances. It mixes with gasoline and other hydrocarbons in all proportions, which the ordinary 95 per cent alcohol is incapable of doing. For commercial purposes alcohol is rendered anhydrous by an **azeotropic distillation method** involving the use of benzene as the "added liquid".

In this process, advantage is taken of the fact that ethyl alcohol, water and benzene form a **ternary mixture having a minimum boiling-point of 64·9°** and containing :

Water,	7·4 per cent.
Alcohol,	18·5 ,, ,,
Benzene,	74·1 ,, ,,

Further, benzene and ethyl alcohol form a **binary mixture having a minimum boilingpoint of 68·°** and containing :

Alcohol,	32·4 per cent.
Benzene,	67·6 ,, ,,

On fractionally distilling aqueous alcohol containing a sufficient proportion of added benzene, the minimum-boiling ternary mixture first passes over, until all the water has been eliminated. Then the binary mixture of alcohol and benzene passes over, until all benzene has been removed. The residual liquid in the still consists of absolute alcohol. The recovered benzene is utilized for the dehydration of a further quantity of alcohol.

16. By-Products of Alcohol Industry.—The important by-products of the alcohol industry are :

(1) **Carbon Dioxide.** During the fermentation, large quantities of carbon dioxide are evolved. The gas is purified and compressed to the liquid state, and is sold either as such or in the solidified form for refrigeration purposes.

(2) **Head Products.** The more volatile constituents (chiefly acetaldehyde and volatile esters) present in the crude spirit pass over as "*first runnings*" or "*head products*" during the fractional distillation of crude spirit, and are collected separately.

(3) **Fusel Oil.** This is obtained as the "*last runnings*" or "*tail products*" during fractional distillation of crude spirit. It consists of an oily mixture of higher alcohols that are only moderately soluble in water. They are not produced from the sugar or starch as was formerly supposed, but by the disruption of certain amino-acids (particularly *leucine*, *isoleucine* and *valine*) present as such in the

natural mash or produced from proteins of the raw material during the conversion of the malt into sugar. The decomposition is brought about by yeast to satisfy its need for nitrogen and for the production of enzymes, the higher alcohols being left behind as non-assimilable products of metabolism. Thus, *l*-leucine (*a*-aminoisobutylacetic acid) gives inactive isoamyl alcohol,

$$(CH_3)_2CH{\cdot}CH_2.CH(NH_2){\cdot}COOH + H_2O \longrightarrow (CH_3)_2CH.CH_2{\cdot}CH_2OH + CO_2 + NH_3$$

Similarly, *l*-isoleucine gives *l*-amyl alcohol, and valine gives isobutyl alcohol.

The proportion of fusel oil in raw spirit is from 0·2 to 0 4 per cent by volume. It may be increased by the addition of leucine and other amino-acids to the fermenting mash.

Fusel oil fetches a much higher price per gallon than the alcohol itself It is chiefly used in the production of the so-called *commercial amyl alcohol* (sec. 22), which has numerous technical applications.

(4) **Spent Wash.** The "spent wash" *i.e.*, the liquid from which the alcohol has been recovered by distillation, contains all the proteins present in the starting material. It is utilized as a cattle feed.

(5) **Argol or tartar.** This consists of crude potassium hydrogen tartrate, which, being insoluble in aqueous alcohol, separates during fermentation of grape-juice, as hard, brown crusts. It serves as the raw material for the manufacture of tartaric acid.

17. Properties of Ethyl Alcohol.—Ethyl alcohol is a colourless mobile liquid, having a pleasant, pungent odour. Absolute alcohol boils at 78·37° and has a sp. gr. of 0·789 at 20°.

Ethyl alcohol forms a constant-boiling mixture with water containing 95·5 per cent of the alcohol and boiling at 78·13°. In dilute solutions, alcohol has a specific intoxicating effect on the system. The use of spirits and liqueurs is based on this property. Alcohol is an excellent solvent for many organic substances, such as resins and oils.

Alcohol burns with a pale blue, non-luminous flame. It possesses the general chemical characters of a primary alcohol.

Nitric acid oxidizes ethyl alcohol with explosive violence, producing among other products, acetaldehyde, carbon dioxide and water.

Constitution. See under chap. 5, sec. 13, p. 74.

Detection. Ethyl alcohol can be readily detected as in the following experiments :

Expt. 4. *Iodoform Test.* Warm a small quantity of ethyl alcohol with a crystal of iodine, and then add a solution of potassium hydroxide, drop by drop, until the iodine colour just disappears. A yellow precipitate of iodoform, possessing a characteristic odour, will separate out, either immediately, or after some time. This test is given by several other compounds including acetone.

Exp. 5. *Ethyl Acetate Test.* Warm some ethyl alcohol with glacial acetic acid and concentrated sulphuric acid, and smell the vapour given off. A pleasant, fruity odour of ethyl acetate will be observed.

18. Estimation of Ethyl Alcohol (*Alcoholometry*).—The percentage of ethyl alcohol in a mixture of pure water and alcohol can be readily determined by noting the specific gravity of the mixture and then looking up the figure in a reference table. For instance, if the specific gravity is found to be 0·8605 at 15·5°, reference to the table would show that the sample contains 75 per cent of alcohol by weight. In the case of beers, wines and spirits, the sugary and other extractive matters present influence the specific gravity to such an extent that a direct determination of specific gravity would be of no value. Hence, a measured quantity of the sample is submitted to distillation, until about one-half has passed over. The distillate, which contains practically the whole of the alcohol, is diluted with pure water to the original volume of the sample, and then the specific gravity of the solution is taken.

19. Uses of Ethyl Alcohol.—

(1) In its various denatured forms, ethyl alcohol is the most extensively used organic solvent. It is used for this purpose in the laboratory, in making pharmaceutical tinctures, and in the preparation of varnishes and lacquers.

(2) It is also used as a *fuel* in spirit lamps and spirit stoves. The use of ethyl alcohol as a **motor fuel** or **power alcohol** has attracted much attention. It is not sufficiently volatile to give proper starting in cold water. This difficulty is overcome by using a mixture containing about 25 per cent of ether or petrol.

(3) Large quantities of ethyl alcohol are used in the production of numerous organic compounds, such as ether, chloroform, dyes, alkaloids, perfumes and collodion.

(4) Ethyl alcohol is also used as a *preservative* of biological specimens and as an *antiseptic* for the skin.

(5) Ethyl alcohol is the essential constituent of alcoholic drinks (such as wine, whisky, brandy etc.), so commonly used as intoxicants.

20. Propyl Alcohols, C_3H_7OH.

***n*-Propyl Alcohol**, *Propanol* 1, $CH_3.CH_2.CH_2OH$ (b p. 97°), occurs in *fusel oil* from which it is obtained by fractionation. It has been extensively used in organic synthesis, but is of no commercial importance.

Isopropyl Alcohol, *Propanol*-2, $CH_3.CH(OH).CH_3$ (b.p. 82°), is manufactured from propylene, obtained as a by-product in the cracking of heavy oils. The process consists in absorbing the hydrocarbon in sulphuric acid,

$$\underset{\text{Propylene}}{CH_3.CH=CH_2} + H_2SO_4 \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{(CH_3)_2CH.HSO_4}$$

and decomposing the resulting ester by the addition of water,

$$(CH_3)_2CH.HSO_4 + HOH \longrightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} + H_2SO_4$$

The gas from the cracking stills, containing about 15 per cent of the olefin hydrocarbons, is treated in towers with 87 per cent sulphuric acid, which absorbs propylene and butylene but not ethylene. The solution is run into warm water, and, after the separation of tarry matter, subjected to fractionation.

Isopropyl alcohol is nowadays used in industries under the name of **Petrohol.** Large quantities are being used in the manufacture of **Isopropyl Acetate** employed as a solvent in lacquers. Petrohol is also used as a solvent in cosmetics and hair tonics, and in the manufacture of acetone.

21. Butyl Alcohols, C_4H_9OH.—There are four isomerio butyl alcohols.

***n*-Butyl Alcohol** or **Butanol-1.** $CH_3.CH_2.CH_2.CH_2OH$. This alcohol is prepared on a large scale from starch by fermentation with *bacillus acetobutylicus*. Carbon dioxide and hydrogen are evolved during the process, and the product consists of butyl alcohol (60 per cent), acetone (30 per cent) and ethyl alcohol (10 per cent). These are separated and purified by fractional distillation.

Large quantities of butyl alcohol are also obtained by the aldol condensation of acetaldehyde. The aldehyde is condensed to aldol and the latter dehydrated to crotonaldehyde in a single continuous process. The crotonaldehyde is then hydrogenated to butyl alcohol in the presence of a nickel-chromium catalyst :—

$$2CH_3.CHO \xrightarrow{\text{Alkali}} \underset{\text{Acetaldol}}{CH_3.CH(OH)\,CH_2.CHO} \xrightarrow{-H_2O} \underset{\text{Crotonaldehyde}}{CH_3.CH{=}CH.CHO}$$

$$CH_3.CH{=}CH.CHO + 2H_2 \xrightarrow{\substack{\text{Ni-Cr}\\ 180^\circ}} \underset{n\text{-Butyl alcohol}}{CH_3.CH_2.CH_2\,CH_2OH}$$

n-Butyl alcohol is used as a solvent in the manufacture of lacquers. Even larger quantities are employed in the manufacture of butyl acetate and other butyl esters, which, too, are important lacquer solvents.

Butanol-2, *Secondary Butyl Alcohol*, $CH_3.CH_2.CH(OH)CH_3$, is prepared by the reduction of methyl ethyl ketone and also from normal butenes (obtained during petroleum cracking). It boils at 100°.

Isobutyl Alcohol, 2-*Methylpropanol, Methylethylcarbinol*, $(CH_3)_2CH.CH_2OH$, occurs in fusel oil, and has been extensively used in organic synthesis.

Tertiary Butyl Alcohol, or *Trimethylcarbinal*, $(CH_3)_3COH$, is obtained from acetone through the Grignard reaction. It is one of the few

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[1] The name suggests the origin (petroleum) and nature (alcohol) of the substance.

lower alcohols that are solid at the ordinary temperature. It melts at 25°C, and boils at 83°C.

22. Amyl Alcohols, $C_5H_{11}OH$.—All the eight isomeric amyl alcohols are known. Of these, four are primary, three secondary, and one tertiary. The so-called **commercial amyl alcohol**, obtained from fusel oil, is a *mixture* of the following two isomers :

(1) $CH_3.CH_2.CH(CH_3)CH_2OH$
2-Methyl-l-butanol
(b.p. 125°)

(2) $(CH_3)_2CH.CH_2.CH_2OH$
3-Methyl-l-butanol
(b.p. 131°)

The former component is known as **active**[1] **amyl alcohol** and the latter **isoamyl alcohol.** For commercial purposes, the mixture is used as such. Large quantities are converted into the corresponding mixture of **amyl acetates**, employed as a solvent in lacquers.

23. C_{12}, C_{16} and C_{18} Alcohols.—The *normal* alcohols, namely **lauryl alcohol**, $C_{12}H_{25}OH$, **cetyl alcohol**, $C_{16}H_{33}OH$, and **stearyl alcohol**, $C_{18}H_{37}OH$, are now of industrial importance, and are used :

(1) as emulsifying agents,

(2) as bases for certain pharmaceutical preparations, and

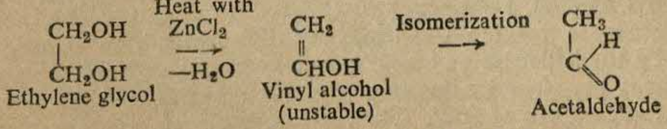
(3) in making detergents.

All these are prepared by the reduction of fats and oils.

UNSATURATED ALCOHOLS

24. The unsaturated alcohols are derived from olefins or acetylenes, and consequently possess the dual character of an alcohol and an unsaturated compound. The olefin alcohols, $C_nH_{2n-1}OH$ or $C_nH_{2n}O$, are isomeric with aldehydes and ketones derived from alkanes.

As in the case of unsaturated halogen derivatives, two distinct classes of olefine alcohols are possible. However, the alcohols in which the OH group is directly united to a doubly bound carbon atom are unknown, since the grouping $>C=CH.OH$ is unstable and readily passes into the group $>CH.CH=O$. An example of this class is **vinyl alcohol**, $CH_2=CHOH$, traces of which are supposed to occur in commercial ether. It has never been isolated, since all reactions which might be expected to produce this substance yield, instead, its isomeride acetaldehyde ; *e.g.*,



25. Vinyl Esters.—Although vinyl alcohol itself is too unstable to exist, its halides and esters are stable substances. The chloride and bromide have already been described (page 211).

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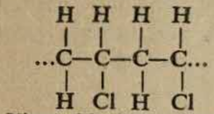
[1] As it is optically active (levorotatory).

Vinyl Acetate, $CH_3COO.CH{=}CH_2$, is manufactured in large quantities by the addition of acetic acid to acetylene in the presence of the mercuric salt of acetylsulphuric acid (catalyst) :

$$CH_3.COOH + HC{\equiv}CH \longrightarrow CH_3COO.CH{=}CH_2$$

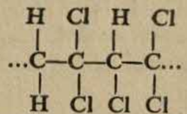
It is one of the key materials for the production of vinyl resins.

26. Vinyl Resins.—As already stated under Vinyl Chloride, (p. 211), the vinyl grouping, $H_2C{=}C{<}$, attached to an electrophylic atom or group is capable of undergoing addition polymerization in the presence of catalysts (ultra-violet light, peroxides, ozone, tetraethyl lead). The resulting high polymers are long, slender molecules in which the monomers are linked together in a head-to-tail fashion, as shown below :—



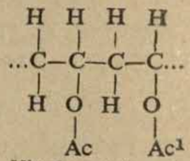
$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ \ldots C- & C- & C- & C\ldots \\ | & | & | & | \\ H & Cl & H & Cl \end{array}$$

Vinyl chloride polymer
(or Polyvinyl chloride)



$$\begin{array}{cccc} H & Cl & H & Cl \\ | & | & | & | \\ \ldots C- & C- & C- & C\ldots \\ | & | & | & | \\ H & Cl & Cl & Cl \end{array}$$

Vinylidine chloride polymer
(or polyvinylidine chloride)



$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ \ldots C- & C- & C- & C\ldots \\ | & | & | & | \\ H & O & H & O \\ & | & & | \\ & Ac & & Ac^1 \end{array}$$

Vinyl acetate polymer
(or Polyvinyl acetate)

The polymerisation increases sharply with the rise of temperature. By the control of various factors, high polymers ranging in molecular weight from 4,000 to 10,000 may be obtained.

Each of the monomers may be polymerized separately. More satisfactory products, however, are obtained by copolymerization of two or more of them in suitable proportions.

Vinyl polymers and copolymers constitute a very important class of **Synthetic Plastics.** They are put to widely varied uses, such as :—

(1) in making rigid sheets and tubing,

(2) flexible sheets and films, draperies, bed-covers, rain-coats, and collapsible bottles, etc.,

(3) moulded articles, such as gramophone records,

(4) protective coatings, including wire and cable coatings and water-proof cloth.

27. Allyl Alcohol, 1-*Propen-3-ol*, $CH_2{=}CH.CH_2OH$.—This compound occurs in minute quantities in raw wood spirit. It may be obtained by the hydrolysis of allyl iodide by means of boiling water, but is usually prepared by heating glycerol with anhydrous oxalic acid to a temperature of 260°. The reaction has been shown to occur in two stages, a glyceryl dioxalate being formed as the intermediate

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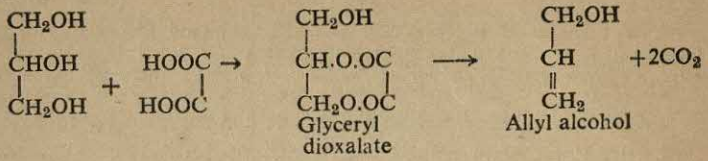
[1] Ac = the acetyl group, $CH_3.CO-$

product, which then gets decomposed by heat into carbon dioxide and allyl alcohol :



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} HOOC \\ | \\ HOOC \end{array} \rightarrow \underset{\text{Glyceryl dioxalate}}{\begin{array}{l} CH_2OH \\ | \\ CH.O.OC \\ | \quad\quad | \\ CH_2O.OC \end{array}} \longrightarrow \underset{\text{Allyl alcohol}}{\begin{array}{l} CH_2OH \\ | \\ CH \\ \| \\ CH_2 \end{array}} + 2CO_2$$

Expt. 6. *Preparation of Allyl Alcohol.* Distil a mixture of 30 gm. of oxalic acid and 100 ml. of glycerol from a retort provided with a thermometer dipping into the liquid. Reject the distillate passing up to 180°, which contains formic acid. Then change the receiver, and collect the liquid distilling up to 280°, which contains allyl alcohol. Redistil this portion until the temperature reaches 105°. Dehydrate distillate with anhydrous potassium carbonate, and then redistil.

Properties. (1) Allyl alcohol is a colourless, pungent-smelling, mobile liquid boiling at 96·7°. It is miscible with water in all proportions.

Allyl alcohol possesses two sets of reactions, (*i*) reactions of an unsaturated compound, and (*ii*) those of a primary alcohol. As an unsaturated compound, it combines directly with hydrogen, halogens and halogen hydrides. When carefully oxidized with alkaline permanganate, two hydroxyl groups are added on, with the production of glycerol :

$$\underset{\text{Allyl alcohol}}{H_2C{=}CH.CH_2OH} + H_2O + O \rightarrow \underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH}$$

As an alcohol, it combines with acids, forming esters ; *e.g.*,

$$CH_3COOH + HOCH_2.CH{=}CH_2 \rightleftharpoons \underset{\text{Allyl acetate}}{CH_3COO.CH_2.CH{=}CH_2} + H_2O$$

(2) When carefully oxidized with silver oxide, the primary alcohol group gets oxidized first to an aldehyde group and then to a carboxyl group :

$$\underset{\text{Allyl alcohol}}{H_2C{=}CH.CH_2OH} \xrightarrow{-2H} \underset{\text{Acraldehyde}}{H_2C{=}CH.CHO} \xrightarrow{+O} \underset{\text{Acrylic acid}}{H_2C{=}CH.COOH}$$

28. Propargyl Alcohol, 1-*Propyn*-3-*ol*, $CH{\equiv}C.CH_2OH$. This is the simplest of the acetylene alcohols. As a compound containing an acetylenic function, it combines directly with four atoms of bromine, and forms explosive metallic derivatives with ammoniacal solutions of cuprous chloride and silver nitrate. It is a pleasant-smelling liquid boiling at 114°.

QUESTIONS

1. What are different classes of monohydric alcohols ? Describe two methods of distinguishing between them.

Starting with ethyl alcohol, how would you prepare (*i*) Methyl alcohol, (*ii*) Propylene, (*iii*) Acetone ? (*Bihar, B.Sc., 1959*)

2. How would you convert a primary alcohol into secondary and tertiary ones ? (*Agra, B.Sc., 1958*)

3. Describe the manufacture of ethyl alcohol from starch. What is the action of chlorine, HCl and sodium on ethyl alcohol? Give equations.
(Calcutta, B.Sc., 1959)

4. A primary alcohol with a V. D. of 29 contained C = 62·1, H = 10·3% and reacted with bromine to give a derivative which contained C = 16·5, H = 2·7 and Br = 73·4%. Determine the structural formula of the compound and its derivative.
(Agra, B.Sc., 1957; Lucknow, B.Sc., 1954)

Ans. Allyl alcohol, $CH_2=CHCH_2OH$; 2, 3-Dibromopropanol-1.

5. 0·2881 gm. of an alcohol, on being added to ethyl magnesium iodide, caused the evolution of 48·33 ml. of ethane at 20° and 755 mm. Calculate the molecular weight of the alcohol.
(*Ans.* 144)

6. The analysis of an organic substance gave the following results: 0·2115 gm., on combustion gave 0·4655 gm. CO_2 and 0·2533 gm. H_2O. The vapour density of the substance was 29·7. When treated with potassium dichromate and dilute sulphuric acid, it produced a substance which gave the iodoform test. What was the original compound?
[*Ans.* *Isopropyl alcohol* $(CH_3)_2CH.OH$].

7. How will you differentiate between a primary, secondary and tertiary alcohol?

Indicate briefly the method for the manufacture of absolute alcohol.
(Lucknow, B.Sc., Prev., 1962)

8. A primary alcohol of density 29 contains carbon 62·1% and hydrogen 10·3%. On reacting with bromine, it yields a derivative that has carbon 16·5%, hydrogen 2·7% and bromine 73·9%. Determine the structural formula of the alcohol.
Ans. $H_2C=CH.CH_2OH$.
(Lucknow, B.Sc., 1954)

9. Describe the preparation and properties of the isomeric butyl alcohols and indicate, by means of equations, how you would convert butanol-1 into (*a*) butanol-2, (*b*) butanediol-1,2 and (*c*) *n*-octane.
(Lucknow, B.Sc., 1962)

10. How will you differentiate between a primary, secondary and tertiary alcohol? What is the relative order of reactivity of primary, secondary and tertiary alcohols (*a*) with hydrochloric acid and zinc chloride (*b*) with PCl_3 to give alkyl chlorides, (*c*) PCl_3 to give phosphorous esters, (*d*) when dehydrated?
(Lucknow, B.Sc., 1962)

11. Describe the methods for the synthesis of isomeric butyl alcohols.
(Lucknow, B.Sc., 1959)

How is absolute alcohol prepared :—

(*a*) in the laboratory.

(*b*) on the commercial scale.
(Lucknow, B.Sc., 1959)

12. Give the structural formulae, names (I.U.C.) and the methods of identification of isomeric butanols.
(Lucknow, B.Sc., 1962)

13. Write a short note on Power alcohol.
(Lucknow, B.Sc., 1960)

14. Outline the methods for the preparation of ethyl alcohol. Describe its chemical reactions and show how they resemble those of water.
(Punjab, B.Sc., Dairying, 1960)

15. (*a*) Discuss "fermentation" with special reference to the manufacture of ethyl alcohol.

(*b*) Compare the properties of ethyl alcohol and phenol.
(Karnatak, B.Sc., 1960)

16. Describe the methods for the synthesis of isomeric butyl alcohols.
(Lucknow, B.Sc., 1960)

17. What do you understand by fermentation? How is ethyl alcohol manufactured from starchy substances? How and under what conditions does it react with (*a*) calcium chloride and (*b*) strong sulphuric acid?
(Pondichery, Pre-Professional, 1960)

18. Describe the fermentation method of manufacture of ethyl alcohol. (*Delhi, B.Sc., 1957*)

19. How are the primary, secondary and tertiary alcohols distinguished by Victor Meyer's method ? (*Agra, B.Sc., 1957*)

20. Describe fully a method of distinguishing the primary, secondary and tertiary alcohols from each other. (*Patna, B.Sc., 1958*)

21. Starting from ethyl alcohol how would you prepare (*a*) ethane, (*b*) ethylene, (*c*) acetylene, (*d*) *n*-butyl alcohol, (*e*) acetone, (*f*) propionic acid ? (*Rangoon, B.Sc., 1958*)

22. How is pure methyl alcohol obtained from pyroligneous acid ? How are the following prepared, starting from methyl alcohol :—

(*a*) ethane, (*b*) methylamine,
(*c*) acetic acid. (*d*) acetamide. (*Mysore, B.Sc., 1960*)

23. Given butanol-1 show how to prepare the following by means of inorganic reagents :

(*a*) Butanol-2. (*b*) Butanediol-1, 2. (*c*) *n*-Octane.
(*d*) Butene-2. (*e*) Isobutene (methylpropene). (*Lucknow, B.Sc., 1956*)

24. Describe the manufacture of ethyl alcohol from molasses. How would you convert ethyl alcohol to (*a*) acetaldehyde and (*b*) ethyl acetate ? (*Travancore, B.Sc. Subs., 1956*)

25. Describe the manufacture of ethyl alcohol from starch materials. How is absolute alcohol prepared ? (*Annamalai, B.Sc., 1951*)

26. Describe the manufacture of ethanol from starch. How is absolute alcohol obtained ? Suggest a test to distinguish absolute alcohol from rectified spirit. (*Baroda, B.Sc., 1962*)

27. How the absolute alcohol is prepared from rectified spirit ? Outline two methods of distinguishing between primary, secondary and tertiary alcohols. (*Saugor, B.Sc., 1962*)

28. What is meant by fermentation ? Describe the preparation of ethyl alcohol and vinegar by this method. (*Utkal, B.Sc., 1962*)

CHAPTER FIFTEEN

ESTERS OF INORGANIC OXY-ACIDS

1. General.—Esters are the compounds produced as the result of reaction between an alcohol and an acid with the simultaneous liberation of water. The esters of halogen hydracids, or *alkyl halides*, have already been described (chapter 12). In this chapter the esters of inorganic oxy-acids will be taken up.

2. General Methods of Formation :—

(1) *From Alcohols.* The esters of inorganic oxyacids may be obtained from the alcohols by the action of acids, acid chlorides or acid anhydrides ; *e.g.*,

(*a*) $$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5.HSO_4 + H_2O$$

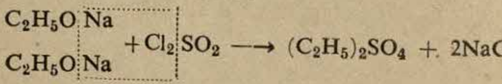
$$C_2H_5HSO_4 + C_2H_5OH \rightleftharpoons (C_2H_5)_2SO_4 + H_2O$$

(*b*) $$2C_2H_5OH + SO_2Cl_2 \rightarrow (C_2H_5)_2SO_4 + 2HCl$$

(*c*) $$2C_2H_5OH + SO_3 \rightarrow (C_2H_5)_2SO_4 + H_2O$$

The reaction of alcohols with acid chlorides or anhydrides is of special importance for the preparation of *normal* esters of polybasic acids.

(2) *From Sodium Alkoxides.* A better method of preparing normal esters of polybasic acids consists in treating sodio-derivatives of alcohols with acid chlorides ; *e.g.*,



$$\begin{array}{l} C_2H_5O\,Na \\ C_2H_5O\,Na \end{array} + Cl_2SO_2 \longrightarrow (C_2H_5)_2SO_4 + 2NaCl$$

(3) *From Alkyl Halides.* When an alkyl halide is distilled with the silver salt of an oxyacid, there occurs a double decomposition between the two, and the ester of the oxyacid passes over ; *e.g*.,

$$C_2H_5I + AgNO_3 \longrightarrow C_2H_5NO_3 + AgI$$

3. Reactions.—The most important reaction of the esters of inorganic oxyacids is their hydrolysis by aqueous alkalis, when the component alcohol is set free ; *e.g.*,

$$C_2H_5NO_3 + NaOH \longrightarrow C_2H_5OH + NaNO_3$$

Acid esters are often hydrolysed merely on being mixed with water at the ordinary temperature ; *e.g.*,

$$C_2H_5HSO_4 + H_2O \rightleftharpoons C_2H_5OH + H_2SO_4$$

The action, however, occurs more readily on boiling.

4. Alkyl Hydrogen Sulphates.—Alkyl hydrogen sulphates, *i.e.*, acid esters of sulphuric acid, are obtained :

(1) from alcohols by action of concentrated sulphuric acid,

(2) from olefin hydrocarbons, by treatment with sulphuric acid of proper concentration.

Alkyl hydrogen sulphates are acidic in reaction, and their metallic salts are mostly soluble in water. The **potassium alkyl sulphates** crystallize well, and, like alkyl halides, are used as **synthesizing agents.** When heated or subjected to dry distillation with suitable reagents, they yield certain classes of organic compounds. Thus,

(1) with potassium bromide, they give alkyl bromides,

$$C_2H_5KSO_4 + KBr \longrightarrow C_2H_5Br + K_2SO_4$$

(2) with potassium hydrosulphide, thio-alcohols,

$$C_2H_5KSO_4 + KHS \longrightarrow C_2H_5SH + K_2SO_4$$

(3) with potassium sulphide, thio-ethers.

$$2C_2H_5KSO_4 + K_2S \longrightarrow C_2H_5.S.C_2H_5 + 2K_2SO_4$$

and (4) with potassium cyanide, alkyl cyanides,

$$C_2H_5KSO_4 + KCN \longrightarrow C_2H_5CN + K_2SO_4.$$

Sodium salts of alkylsulphuric acids derived from higher alcohols, containing ten or more carbon atoms in the alkyl group, possess soap-like properties, and are extensively used as detergents.

5. Ethyl Hydrogen Sulphate, *Ethylsulphuric acid*, $C_2H_5HSO_4$. This is the most important representative of its class, and is obtained by the interaction of ethyl alcohol and concentrated sulphuric acid.

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O$$

The yield is never quantitative, as the reaction attains an equilibrium

Expt. 1. *Preparation of Ethyl Hydrogen Sulphate.* A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated for about one hour on a steam bath under a reflux condenser. The reaction mixture is cooled, diluted with water, and treated with barium carbonate to neutralize the unchanged sulphuric acid and to convert ethyl hydrogen sulphate into barium ethyl sulphate. The barium sulphate and the excess of barium carbonate are filtered off and the *solution of barium ethyl sulphate* is treated with cold dilute sulphuric acid, until the precipitation of barium sulphate is complete :

$$(C_2H_5SO_4)_2Ba + H_2SO_4 \longrightarrow 2C_2H_5HSO_4 + BaSO_4$$

The solution is once again filtered to remove barium sulphate, and then evaporated at the room temperature under reduced pressure. Water and alcohol pass off, while ethyl hydrogen sulphate remains behind as a thick sour liquid.

Ethyl hydrogen sulphate is an odourless oily liquid. It has a strongly acidic reaction, and is miscible with water in all proportions. The more important reactions of ethyl hydrogen sulphate are :

(1) The aqueous solution of the ester undergoes hydrolysis, yielding free sulphuric acid and ethyl alcohol, the reaction being slow at the ordinary temperature. Decomposition of ethyl hydrogen sulphate (obtained from ethylene) with steam is employed in the manufacture of ethyl alcohol.

(2) Ethyl hydrogen sulphate forms readily soluble metallic salts, of which the potassium salt is the most important and is used in the synthesis of certain ethyl compounds (sec. 4).

(3) When heated alone, it yields free sulphuric acid and diethyl sulphate :

$$2C_2H_5HSO_4 \longrightarrow (C_2H_5)_2SO_4 + H_2SO_4$$

At the same time, free sulphuric acid and ethylene are produced :

$$C_2H_5HSO_4 \rightleftharpoons C_2H_4 + H_2SO_4$$

(4) When it is heated with alcohol, diethyl ether, $C_2H_5.O.C_2H_5$, is obtained :

$$C_2H_5HSO_4 + C_2H_5OH \longrightarrow C_2H_5.O.C_2H_5 + H_2SO_4$$

6. Dimethyl and Diethyl Sulphates, $(CH_3)_2SO_4$ and $(C_2H_5)_2SO_4$.—These two very important esters of sulphuric acid are prepared on a commercial scale by distilling the theoretical quantity of sulphur trioxide into well cooled methyl or ethyl alcohol :—

$$2CH_3OH + 2SO_3 \longrightarrow (CH_3)_2SO_4 + H_2SO_4$$
$$2C_2H_5OH + 2SO_3 \longrightarrow (C_2H_5)_2SO_4 + H_2SO_4$$

Dimethyl sulphate is also prepared by the vacuum distillation of **methyl hydrogen sulphate**[1],

$$2CH_3HSO_4 \rightleftharpoons (CH_3)_2SO_4 + H_2SO_4.$$

Dimethyl and diethyl sulphate are colourless liquids. The former boils at 187° at the atmospheric pressure and the latter at 96° at 15 mm. They are both **highly piosonous**, and cause burns on the skin and attack mucous membranes of the respiratory system.

Methyl and ethyl sulphates are used both in the laboratory and on a commercial scale as **methylating and ethylating agents** respectively. They are preferred, for this purpose, to methyl and ethyl iodides as they are much cheaper and give better yields. They are of particular interest for the alkylation of primary and secondary amines and for the etherification of phenols.

7. Ethyl Nitrate, $C_2H_5NO_3$.—When ethyl alcohol is treated with concentrated nitric acid, the oxidation of the alcohol occurs more rapidly than esterification. Further, the oxides of nitrogen produced in the reaction attack the alcohol, yielding ethyl nitrite. The reaction is highly exothermic, and, unless proper care is taken, may become almost explosive in violence.

To overcome this difficulty, a little urea is added to the well-cooled reaction mixture, which decomposes the nitrous acid formed,

$$\underset{\text{Urea}}{NH_2CO.NH_2} + \underset{\text{Nitrous acid}}{2HNO_2} \longrightarrow 2N_2 + CO_2 + 3H_2O,$$

and thus prevents the formation of ethyl nitrite. Further, in the presence of urea, the reaction takes place quietly, and ethyl nitrate is the principal product.

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[1] **Methyl hydrogen sulphate** is commercially obtained by the interaction of methyl alcohol and fuming sulphuric acid.

Expt. 2. *Preparation of Ethyl Nitrate.* Place 15 ml. of nitric acid (sp. gr. 1·4) and about 5 grams of urea in a large-size, round-bottom flask. Cool the flask with ice, and add gradually to the mixture 30 ml. of ethyl alcohol. When all the alcohol has been added, attach a Liebig condenser to the flask, and heat it *very slowly* on water bath. Wash the distillate (consisting of the ester and unused alcohol and acid) with water in a separating funnel. Dry the ester layer with fused calcium chloride, and redistil the dry ester from a water-bath.

Ethyl nitrate may also be obtained by the double decomposition between an alcoholic solution of silver nitrate and ethyl iodide :

$$C_2H_5I + AgNO_3 \longrightarrow C_2H_5NO_3 + AgI$$

Ethyl nitrate is a colourless liquid having a sp. gr. of 1·1 and boiling at 87°. It has a pleasant odour, is practically insoluble in water but is readily soluble in alcohol or ether. It burns with a luminous flame, and, if thrown on a hot surface, may explode. It is hydrolysed by boiling water and hot alkalis. On reduction with tin and hydrochloric acid, it gives *hydroxylamine* NH_2OH :—

$$C_2H_5NO_3 + 6H \longrightarrow C_2H_5OH + NH_2OH + H_2O$$

8. Esters of Nitrous Acid.—Esters of nitrous acid, or *alkyl nitrites*, are prepared by the action of nitrous anhydride (nitrogen trioxide) on alcohols ; *e.g.*,

$$2C_2H_5OH + N_2O_3 \longrightarrow \underset{\text{Ethyl nitrite}}{2C_2H_5O.NO} + H_2O.$$

A well-cooled mixture of the alcohol and concentrated sulphuric acid is slowly added to a well-cooled solution of sodium nitrite in water. After the reaction is over, the oily layer of ester is separated, washed, dried and distilled.

Properties and Uses. (1) Alkyl nitrites are colourless, very volatile liquids with a stupefying odour.

(2) They are readily hydrolysed to give free nitrous acid,

$$C_2H_5\boxed{O.NO + H}OH \longrightarrow C_2H_5OH + HO.NO$$

For this reason, they are used, in alcoholic solution, as a source of nitrous acid for the preparation of nitroso-compounds and diazonium salts.

(3) When reduced with tin and hydrochloric acid, they get decomposed into the alcohol and hydroxylamine or ammonia,

$$C_2H_5O.NO + 4H \longrightarrow C_2H_5OH + NH_2OH$$
$$C_2H_5O.NO + 6H \longrightarrow C_2H_5OH + NH_3 + H_2O$$

(4) Alkyl nitrites have a very pronounced physiological action; they accelerate the pulse and lower the blood pressure. For this reason, **ethyl nitrite** and **amyl nitrite** are used in medicine for the treatment of asthma and certain heart troubles. Amyl nitrite is perhaps the most effective antidote for cyanide poisoning.

Structure. The structure of alkyl nitrites, as $R{-}O{-}N{=}O$, follows from reactions (2) and (3) given above.

9. **Nitro-paraffins.**—These are isomeric with alkyl nitrites, and are discussed in chapter 28.

QUESTIONS

1. Give the general methods for the preparation of esters of inorganic oxyacids.

2. Describe the preparation of ethylsulphuric acid, and give its important reactions. To what use is its potassium salt put in synthetic chemistry ?

3. Given sulphuric acid and alcohol, what compounds can be prepared ? Give practical details.

4. How are dimethyl and diethyl sulphates prepared ? To what use are they put in organic synthesis ?

5. Describe the preparation of a pure sample of ethyl nitrate in the laboratory. What happens when the ester is subjected to reduction by means of tin and hydrochloric acid ?

6. Describe the separate action of chlorine, sulphuric acid, nitric acid, and nitrous acid on ethyl alcohol. (*Punjab, B.Sc., 1924*)

7. How would you prepare ethyl nitrite ? (*Punjab, B.Sc., 1939*)

8. Describe the preparation and uses of dimethyl sulphate. (*Madras, B.Sc., 1955*)

CHAPTER SIXTEEN

ETHERS

1. General.—Organic compounds in which two alkyl radicals are joined together through an oxygen atom are called **ethers.** The type formula for ethers R.O.R′, in which the alkyl radicals R and R′ may be the same or different. In the former case, the ether is said to be a *simple* ether and in the latter a *mixed* ether. Simple ethers are usually named after the alkyl radical they contain; though sometime the prefix *di-* is also added. Thus, $C_2H_5.O.C_2H_5$ is called *ethyl ether* or *diethyl ether.* For mixed ethers, the name includes both the radicals, the smaller being given first. Thus, $CH_3.O.C_2H_5$ is named *methyl ethyl ether.*

Ethers possess the same general molecular formula as the alcohols, *viz.*, $C_nH_{2n+2}O$.

2. Formation.—Ethers may be prepared by the following general methods :—

(1) **From Alcohols :**

(*i*) *By heating with Concentrated Sulphuric Acid.* This reaction is of great practical importance, and will be described in detail in the case of ethyl ether.

(*ii*) *By Catalytic Dehydration.* In this method, the alcohol vapour is passed over precipitated alumina heated at 240° to 260° :

$$2C_2H_5OH \longrightarrow C_2H_5.O.C_2H_5 + H_2O$$

(2) **From Alkyl Halides :**

(*i*) *By heating with Sodium Alkoxides* **(Williamson's Synthesis) :**

$$\boxed{C_2H_5I + \qquad Na}\underset{\text{Sodium ethoxide}}{O.C_2H_5} \longrightarrow \underset{\text{Ethyl ether}}{C_2H_5.O.C_2H_5} + NaI$$

This method is of great interest, since it shows very clearly the structure of ethers. Moreover, it affords a simple method of synthesizing any desired ether, simple or mixed. Thus, methyl ethyl ether may be obtained by heating a mixture of methyl iodide and sodium ethoxide or of ethyl iodide and sodium methoxide.

(*ii*) *By heating with Silver Oxide* :

$$2C_2H_5I + Ag_2O \longrightarrow C_2H_5.O.C_2H_5 + 2AgI$$

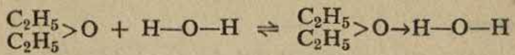
3. Physical Properties.—With the exception of dimethyl ether, which is gaseous at ordinary temperatures, the aliphatic ethers are colourless, mobile, and volatile liquids having a pleasant odour. They are highly inflammable and are lighter than water.

The boiling points of ethers are much lower than those of corresponding alcohols, but are close to the boiling points of hydrocarbons having approximately the same molecular weight, as will appear from the following table :

	Molecular Weight	Boiling Point
Propane, $CH_3.CH_2.CH_3$	44	−42°C
Dimethyl ether, $CH_3.O.CH_3$	46	−25°C
Ethanol, $CH_3.CH_2.OH$	46	+78°C

These figures show that ethers, unlike alcohols, are not "associated liquids". The bonding of the oxygen of one ether molecule with hydrogen of a second ether molecule to form a co-ordinate link is not here possible, as all the hydrogen atoms are linked to carbon, which is not sufficiently electronegative.

Ethers are partially miscible with water. This is due to co-ordination of the oxygen atom of the ether molecule with hydrogen of water :



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O + H{-}O{-}H \rightleftharpoons \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O{\rightarrow}H{-}O{-}H$$

The solubility in water becomes much pronounced in compounds containing more than one ether linkage ; some of these are completely miscible with water.

4. **Chemical Properties.**—Ethers are among the least reactive organic substances. They **do not react** with most of the reagents commonly used in organic chemistry such as :—

(*i*) Alkali metals (in fact metallic sodium is used to dry ethers);

(*ii*) Alkalis ;

(*iii*) Phosphorus pentachloride (and trichloride) ;

(*iv*) Oxidizing agents, such as permanganates and dichromates (*see*, however, Reaction 3, given below).

The non-reactivity of ethers with reagents (*i*), (*iii*) and (*iv*) *differentiates them from alcohols.*

The only **reactions of interest** that ethers undergo are :—

(1) **Formation of Oxonium Salts.** Ethers dissolve in cold, concentrated mineral acids. On diluting the product without allowing the temperature to rise, as by pouring the reaction product upon crushed ice, the ether separates out unchanged. The dissolution of ethers in cold, concentrated acids has been shown to be due to the formation

of electrovalent[1] oxonium salts. Thus, ethyl diether and concentrated sulphuric acid give **diethyloxonium sulphate** :—

$$\underset{\text{Diethyl ether}}{(C_2H_5)_2O} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H^+HSO_4^-} \rightleftharpoons \underset{\substack{\text{Diethyloxonium sulphate}\\ \text{(electrovalent)}}}{[(OC_2H_5)_2O\rightarrow H]^+HSO_4^-}$$

Similarly, diethyl ether and concentrated hydrochloric acid give **diethyloxonium chloride**,

$$(C_2H_5)_2O + H^+Cl^- \rightleftharpoons [(C_2H_5)_2O\rightarrow H]^+Cl^-$$

(2) **Cleavage of the C—O—C chain.** The C—O—C chain is *not* hydrolysed by alkalis (distinction from esters and acid anhydrides). The most effective method of cleavage is **treatment with hydrogen iodide.** The reaction occurs in two stages :—

(*i*) In the *cold*, one equivalent of HI reacts slowly, giving an alkyl iodide and an alcohol :—

$$CH_3—O—C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

With a mixed ether, it is the *smaller* group that forms the iodide.

(*ii*) On *heating with an excess* of the reagent (which is the usual method of effecting cleavage), the alcohol formed is also esterified :

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

The reaction is of importance in the **determination of structure of ethers.**

(3) **Peroxide Formation.** Though unaffected by ordinary oxidizing agents, such as permanganates and dichromates, ethers on prolonged standing in contact with air (as in partially filled containers) absorb oxygen to form small quantities of unstable peroxides (derivatives of hydrogen peroxide having the —O—O— linking). These are liable to decompose on heating with explosive violence. Hence a **dangerous explosion may occur on distilling ether** stored in partially filled containers.

Before distilling an ether, therefore, the sample must first be tested with an acidified solution of potassium iodide and starch solution. The production of blue colour shows the presence of peroxides. Alternatively, a mixture of *pure* ferrous sulphate and potassium sulphocyanide solution (colourless) may be used ; red coloration will develop if peroxides are present. In order to **eliminate peroxides,** the ether is treated with a reducing agent (a solution of ferrous sulphate or sodium bisulphite before distilling). In **storing ether,** it is an advantage to add iron wire, as it inhibits peroxide formation.

5. Constitution.—The constitution of ethers as alkyl oxides follows from Williamson's synthesis, and is supported by their reactions.

6. Identification and Estimation.—Ethers, like hydrocarbons, are characterized by their insolubility in water and their non-reactivity towards common reagents, *viz.*, (*i*) Litmus, (*ii*) Metallic sodium

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[1] That the oxonium salt is highly ionised is shown by the fact that the freezing point lowering of a solution of ether in concentrated sulphuric acid is almost twice as much as could be expected from the number of dissolved ether molecules

(*iii*) Alkalis, (*iv*) Sodium bisulphite, (*v*) Fehling solution and (*vi*) Ferric chloride. To **distinguish an ether from a hydrocarbon**, a few drops of the sample are shaken with cold, concentrated sulphuric acid ; if soluble, the substance under examination is an ether.

In order to determine the constituent alkyl (or aryl) groups present in an ether, the sample is **heated with an excess of hydriodic acid** and the alkyl (or aryl) iodide or iodides are identified by reference to Tables of Physical Constants. Final identification is based on close agreement of at least two physical constants with values given in the Tables.

In general, it is hard to obtain suitable derivatives of ethers, unless the molecule also contains a more reactive functional group besides the ether linkage.

Many complex ethers (*e.g., anethole and eugenol*) occur in nature as components of certain essential oils. These are mixed ethers containing (*i*) a methyl group, and (*ii*) a complex aromatic group. The methyl group or the methoxyl group in these compounds can be estimated by **Zeisel's method**, which consists in heating the compound with hydriodic acid :

$$R(OCH_3)_n + nHI \longrightarrow R(OH)_n + nCH_3I$$

The resulting alkyl iodide is passed into a solution of silver nitrate in 90 per cent alcohol, and the precipitated silver iodide is filtered and weighed. An alternative method consists in decomposing the alkyl iodide by heat, absorbing the iodine thus set free in an aqueous solution of potassium iodide and titrating against standard thiosulphate.

7. Ethyl Ether, $C_2H_5.O.C_2H_5$, **Diethyl Ether.**—Diethyl ether, commonly called "*ether*", is the most important member of the series.

Preparation. Ethyl ether is prepared both technically and in the laboratory by heating a mixture of ethyl alcohol and concentrated sulphuric acid at 140°. The reaction has been shown to proceed in two stages :

$$(1)\qquad \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \rightleftharpoons \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5.HSO_4} + H_2O$$

$$(2)\qquad C_2H_5.HSO_4 + C_2H_5OH \rightarrow \underset{\text{Ethyl ether}}{C_2H_5.O.C_2H_5} + H_2SO_4$$

The ethyl hydrogen sulphate, produced in the first stage of the reaction, reacts with more of the alcohol, producing ether and regenerating sulphuric acid. The latter then acts once again with a further quantity of alcohol, producing more of ethyl hydrogen sulphate and ether. The process is, therefore, *continuous*, and theoretically a small amount of sulphuric acid will etherify an unlimited quantity of alcohol. Actually, however, side reactions take place and the acid is gradually destroyed, owing to its reduction to sulphur dioxide.

Expt. 1. Preparation of Ethyl Ether. The apparatus employed for the preparation of ether is shown in Fig 1 A half-litre distillation flask is fitted with dropping funnel and a thermometer. Its side tube is attached to a long condenser, the lower end of which is fitted into the neck of a second distillation flask to act as the receiver. A long rubber tube is attached to the side tube of the receiver to carry off the ether vapour into the sink. This arrangement prevents the ether vapour from catching fire.

50 ml. of concentrated sulphuric acid are gradually added, with constant shaking, to 100 ml. of alcohol contained in the distillation flask. The latter is then heated on a sand bath, until the temperature rises to about 140°, when ether begins to distil over. Alcohol is now run in, from the dropping funnel, at nearly the same rate as that of the distillation, the temperature being maintained at 140°.

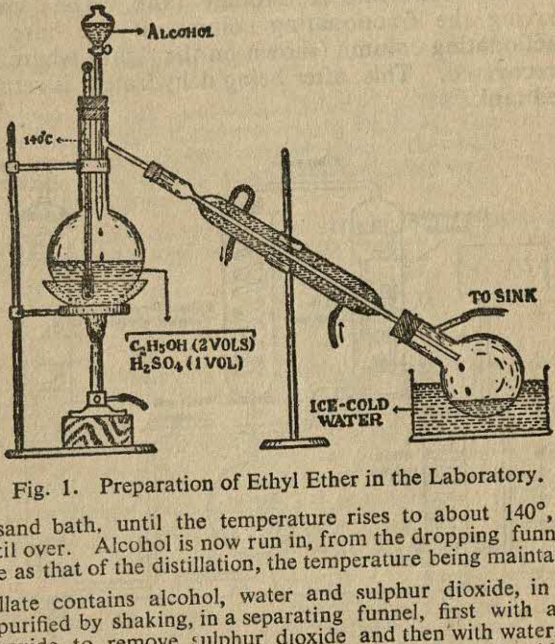


Fig. 1. Preparation of Ethyl Ether in the Laboratory.

The distillate contains alcohol, water and sulphur dioxide, in addition to ether. It is purified by shaking, in a separating funnel, first with a solution of sodium hydroxide to remove sulphur dioxide and then with water. The upper ethereal layer is separated and dried over anhydrous calcium chloride. It is then redistilled from a water bath, when pure ether passes over at 34°—35°C.

The etherification of alcohol can be made really continuous by using, in the above process, syrupy phosphoric acid instead of concentrated sulphuric acid, as unlike the latter, the former is not a reducible compound.

8. Manufacture of Ethyl Ether.—Ether is manufactured by the same reaction as used in the laboratory preparation. The plant shown in Fig. 2 allows production of an unlimited amount of ether from one charge of acid. Pure, concentrated sulphuric acid is introduced into the ether generator shown on the left side of the diagram ; the required quantity of alcohol is then added, and the mixture allowed to stand, when ethyl hydrogen sulphate is produced. The temperature is then raised to 130° and maintained at that level by means of superheated steam passing through a coil immersed in the reaction mixture. A slow, continuous steam of alcohol enters the generator from the alcohol feed tank placed at a higher level. The vapours leaving the generator at the top consist of ether, alcohol, water and traces of sulphur dioxide. They first pass up the alkali scrubber, where sulphur dioxide is removed by means of a solution of sodium hydroxide. Next, they enter a fractionating column, where a separation of ether vapour on the one hand and alcohol-water mixture on the other occurs. The ether vapour leaving at the top of the column is condensed in a water-cooled condenser, and the liquid ether led into a storage tank. The water-alcohol mixture leaving the fractionating column at the base is taken to another fractionating column (shown on the right), where 90 per cent alcohol is recovered. This, after being dehydrated, is returned to the alcohol feed tank.

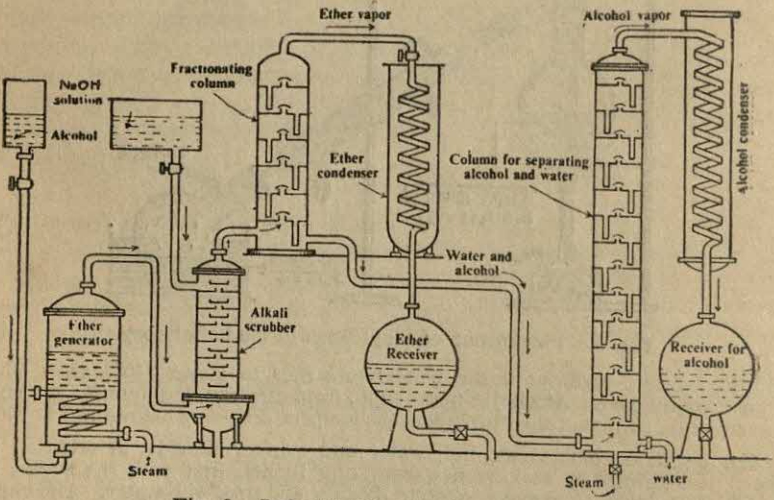


Fig. 2. Industrial Preparation of Ether.

9. Properties of Ethyl Ether.—Ethyl ether is a colourless, mobile and highly volatile liquid boiling at 35·5°. It is only slightly soluble in water (1 vol. in 11 vols. at 25°).

10. Uses of Ethyl Ether.—(1) Ethyl ether is a very valuable *solvent* and crystallizing medium for many organic compounds, and is utilized for extracting aqueous solutions. It is employed on a very large scale in the manufacture of collodion and chardonnet silk.

(2) It is most frequently used as an *anaesthetic* in surgery.

(3) A mixture of alcohol and ether is used in place of petrol as a *motor fuel.*

(4) Ether provides a very suitable *inert medium* for carrying out certain organic reactions, notably the Wurtz's reaction and the Grignard's reaction.

11. Methyl Ether, $CH_3—O—CH_3$.—This ether is nowadays manufactured by passing the vapour of methyl alcohol over heated thoria (or alumina). It is an excellent refrigerant, as it can be allowed to come in direct contact with foodstuffs during **"quick freezing"** without affecting their taste or odour. It is also employed as a low-temperature solvent (b.p., —24°).

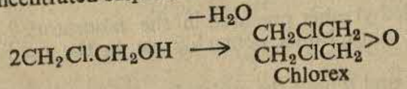
12. Isopropyl Ether, $(CH_3)_2CH—O—CH(CH_3)_2$.—Isopropyl ether is obtained as a by-product in the conversion of propylene to isopropyl alcohol It boils much higher (68°) than ethyl ether, and is therefore less hazardous to handle.

Uses. (1) Isopropyl ether is cheaper than ethyl ether, and is used in preference to the latter for the extraction of certain organic substances (*e.g.*, acetic acid and lactic acid) from dilute aqueous solutions, and is more efficient than ethyl ether.

(2) When mixed with gasoline, it produces a motor fuel of high antiknock value.

13. *n*-Buty Ether (b.p. 142°) and ***n*-Amyl Ether** (b.p. 188°) are now prepared on a commercial scale from the corresponding alcohols. Like isopropyl ether, they are used as solvents in preference to ethyl ether. They have the advantages of much higher boiling points and practical insolubility in water. This means less loss in handling and less danger of fire.

14. Chlorex, β, β′-*dichlorodiethyl ether*, is prepared from ethylene chlorohydrin by heating with concentrated sulphuric acid at 100° :

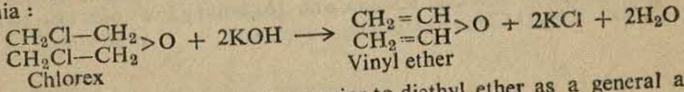


$$2CH_2Cl.CH_2OH \xrightarrow{-H_2O} \begin{array}{l}CH_2ClCH_2\\ CH_2ClCH_2\end{array}\!\!>O$$

Chlorex

It is used as a selective solvent for the production of high-grade lubricating oils. Certain impurities present in the lubricating oils obtained by fractionation of certain crudes impart the objectionable qualities of sludging, oxidation and carbon formation. These impurities are not removable by distillation, but are dissolved out by treatment with Chlorex. An additional advantage of chlorex treatment of lubricating oils is that the viscosity of the product is not so much affected by change of temperature as in the case of oils not so treated.

15. Vinyl Ether, $CH_2=CH—O—CH=CH_2$, (b.p. 28°) is prepared on a large scale by heating chlorex with fused KOH at about 220° in a stream of ammonia :



$$\begin{array}{l}CH_2Cl—CH_2\\ CH_2Cl—CH_2\end{array}\!\!>O + 2KOH \longrightarrow \begin{array}{l}CH_2=CH\\ CH_2=CH\end{array}\!\!>O + 2KCl + 2H_2O$$

Chlorex Vinyl ether

Vinyl ether has been found to be superior to diethyl ether as a general anaesthetic. It acts faster, produces less excitement, and affects the heart less. Further, the recovery from its effect is more rapid.

QUESTIONS

1. Outline the general methods available for the preparation of aliphatic ethers. What reactions do they undergo with (*a*) a dilute mineral acid, (*b*) hydriodic acid, and (*c*) phosphorus pentachloride ? (*Osmania, B.Sc., 1953*)

2. How may diethyl ether be prepared ? What are its properties and uses ? How would you establish the constitution of an ether ? (*Utkal, B.Sc., 1955*)

3. Describe the preparation and purification of diethyl ether by the continuous process. How has the structure of diethyl ether been ascertained ? (*Gauhati, B.Sc., 1955*)

4. How would you prepare a pure specimen of diethyl ether ? What is its action on (*a*) sodium, (*b*) hydriodic acid, (*c*) phosphorus pentachloride in the cold and hot ? Discuss its structure. (*Rangoon, B.Sc , 1956*)

5. Write the formulae of the various ethers having the empirical formula $C_5H_{12}O$. State how would you prepare only one of the isomerides and outline a method for the preparation of the necessary alcohol. (*Nagpur, B.Sc., 1957*)

6. The analysis of an organic substance gave the following results. 0·2115 gm. on combustion gave 0·4655 gm. CO_2 and 0·2533 gm. H_2O. The vapour density of the substance was 29·7. The compound failed to react with metallic sodium, and, on being distilled with hydriodic acid, gave methyl iodide, ethyl iodide and ethyl alcohol. What is the substance ? (*Ans. Methyl ethyl ether*)

7. An organic substance is found to contain C=52·2%. H=13%. C=34·8%. 0·069 gm. of the substance displaced 33·6 ml. of air when measured at N.T.P. The substance reacts neither with sodium nor with phosphorus pentachloride in the cold. What is the substance ? (*Ans. Dimethyl ether*, $(CH_3)_2O$)

8. In Zeisel's determination for methoxyl groups one gm. of a substance of the formula $C_4H_8O_2$ gave, after treatment with red phosphorus, iodine and water and the decomposition of the resulting methyl iodine with alcoholic silver nitrate, 2·67 gm. of AgI. Calculate how many methoxyl groups are present in the molecule. (*Ans. One*) (*Punjab, B.Sc.*)

9. How is diethyl ether prepared and purified in the laboratory ? State its chief properties and uses. (*Calcutta, B.Sc., 1959*)

10. Describe with a sketch the preparation of pure and dry ether in the laboratory. Prove its structure by a simple synthesis. (*Patna, B.Sc., 1958*)

11. How is pure diethyl ether prepared in the laboratory ? What is its action on (*a*) sodium, (*b*) phosphorus pentachloride in the cold and in the hot, (*e*) hydriodic acid.

Two compounds *A* and *B* have the molecular formula C_3H_8O. *A* reacted with hydriodic acid to give C_3H_7I. *B* reacted with hydriodic acid to give methyl iodide as one of the products. Deduce the probable structures of *A* and *B*. (*Rangoon, B.Sc., 1958*)

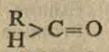
12. How will you obtain ethers ? Describe their general reactions. A compound has the molecular formula $C_4H_{10}O$. How would you show whether it was an alcohol or an ether ? (*Punjab* (*Pakistan*) *B.Sc., 1961*)

13. Two different volatile substances gave the following results on analysis : C, 52·2; H, 13·0; O, 34·8% (by difference). The vapour density of each substance was found to be 23. Assign structural formulae to these two substances. What is the action of (*a*) metallic sodium, and (*b*) boiling hydriodic acid on each of them. (*Ans.* $CH_3.O.CH_3$; C_2H_5OH) (*Calcutta, B.Sc., 1954*

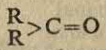
CHAPTER SEVENTEEN

ALDEHYDES AND KETONES

1. General.—Aldehydes and ketones constitute two isomeric series of carbon compounds possessing the general molecular formula, $C_nH_{2n}O$. Both contain the divalent **carbonyl group,** $>CO$, which in the case of aldehydes is linked on the one hand to an alkyl radical and on the other to hydrogen, while in ketones it is linked to two alkyl groups. If the two alkyl groups be identical, the ketone is termed a *simple* ketone, and if they are different, it is called a *mixed* ketone.


$\genfrac{}{}{0pt}{}{R}{H}{>}C=O$

Aldehyde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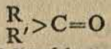
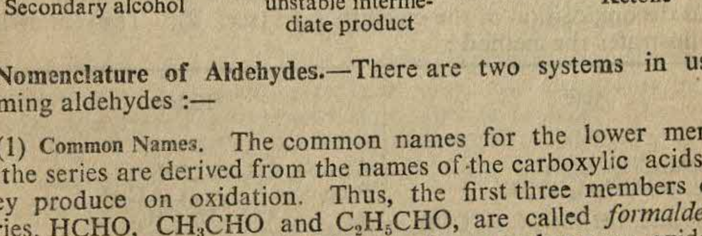
Simple ketone


$\genfrac{}{}{0pt}{}{R}{R'}{>}C=O$

Mixed ketone

Aldehydes and ketones are oxidation products of primary and secondary alcohols respectively, being derived from these by the removal of two hydrogen atoms. The change may be supposed to take place in two stages. In the first instance, an oxygen atom is added, with the production of a compound having two hydroxyls linked to the same carbon atom. This compound, since it is unstable, immediately loses a molecule of water, yielding an aldehyde or a ketone :


$$R.CH_2OH \xrightarrow{+O} R.CH(OH)_2 \xrightarrow{-H_2O} R.C{\genfrac{}{}{0pt}{}{\leqslant H}{\leqslant O}}$$

Primary alcohol — unstable intermediate product — Aldehyde

$$\genfrac{}{}{0pt}{}{R}{R'}{>}CHOH \xrightarrow{+O} \genfrac{}{}{0pt}{}{R}{R'}{>}C(OH)_2 \xrightarrow{-H_2O} \genfrac{}{}{0pt}{}{R}{R'}{>}CO$$

Secondary alcohol — unstable intermediate product — Ketone

Nomenclature of Aldehydes.—There are two systems in use for naming aldehydes :—

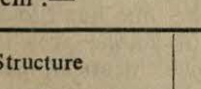
(1) **Common Names.** The common names for the lower members of the series are derived from the names of the carboxylic acids that they produce on oxidation. Thus, the first three members of the series, $HCHO$, CH_3CHO and C_2H_5CHO, are called *formaldehyde*, *acetaldehyde* and *propionaldehyde*, as they produce, on oxidation, formic acid, acetic acid and propionic acid respectively. Similarly, *butyraldehyde*, $CH_3.CH_2.CH_2.CHO$, and *isobutyraldehyde*, $(CH_3)_2CH.CHO$ are named after butyric acid and isobutyric acid.

In naming substituted aldehydes, the position of the substituents on the chain is defined by Greek letters, α, β, γ, δ etc. The first carbon atom behind the aldehyde group is the alpha-carbon atom, the next one beta and so on. Thus, the aldehyde with the structure $(CH_3)_2CH\ CH_2CHO$, *i.e.*, $CH_3.CH(CH_3)CH_2CHO$, is called β-methylbutyraldehyde.

(2) **I.U.C. or Geneva System.** In this system, an aldehyde is named after the *hydrocarbon* from which it is derived, the characteristic suffix of the hydrocarbon name being replaced by the suffix -al (the first two letters of the term *aldehyde*). The following table illustrates the system :—

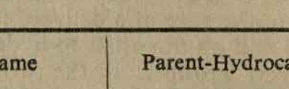
Structure	Geneva Name	Parent-Hydrocarbon
$H.CHO$	Methanal	Methane
$CH_3.CHO$	Ethanal	Ethane
CH_3CH_2CHO	Propanal	Propane
$CH_2=CH.CHO$	Propenal	Propene
$CH\equiv C.CHO$	Propynal	Propyne

In the case of a branch chain aldehyde, the name is derived from **the longest chain containing the aldehyde group**, even though it is not the longest carbon chain in the molecule. The side-chains are located by numbering the carbon atoms of the reference chain, **starting from the carbon atom of the —CHO group.** The following are illustrative examples :—



$\overset{4}{C}H_3.\overset{3}{C}H_2.\underset{\substack{|\\ CH_3}}{\overset{2}{C}H}.\overset{1}{C}HO$

2-Methylbutanal



$\overset{5}{C}H_3.\overset{4}{C}H_2.\overset{3}{C}H_2.\underset{\substack{|\\ {}^1CHO}}{\overset{2}{C}H}.CH_2.CH_3$

2-Ethylpentanal

Nomenclature of Ketones.—There are three systems in use :—

(1) **Common Names for Simple Ketones.** *Simple* ketones are usually named after the acid from which they could be obtained by the thermal decomposition of the calcium salt (sec. 2). The following table illustrates the method :

Acid	Ketone
Acetic acid, CH_3COOH	Acetone, $CH_3.CO.CH_3$
Propionic acid, C_2H_5COOH	Propionone, $C_2H_5.CO.C_2H_5$
n-Butyric acid, $CH_3.CH_2.CH_2COOH$	Butyrone, $\genfrac{}{}{0pt}{}{CH_3CH_2.CH_2}{CH_3CH_2.CH_2}{>}CO$
Isobutyric acid, $(CH_3)_2CH.COOH$	Isobutyrone, $(CH_3)_2CH.CO.CH(CH_3)_2$
Stearic acid, $C_{17}H_{35}COOH$	Stearone, $(C_{17}H_{35})_2CO$

(2) **Alkyl Names.** A more general method, applicable to simple as well as mixed ketones, is to name the alkyl groups attached to the —CO— group, and call the compound a *ketone*. Thus, we have :

Dimethyl ketone, $CH_3—CO—CH_3$
Methyl ethyl ketone, $CH_3—CO—CH_2—CH_3$
Ethyl isopropyl ketone, $CH_3—CH_2—CO—CH(CH_3)_2$

(3) **I.U.C. or Geneva System.** This system is of most general application and is used in all modern literature for naming ketones of more complex structure. Here the reference chain is the **longest possible carbon chain** in which the positions of the —CO—and the alkyl groups present is defined by numerals, and the **position 1 is assigned to the end carbon atom nearest to a —CO— group.** The name is derived from the parent *hydrocarbon*, and number of —CO— groups present in the molecule is indicated by the suffix **-one, -dione, -trione**, etc. The following are some illustrative examples :—

$CH_3.CO.CH_3$
Propanone

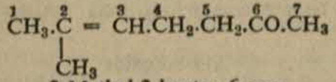
$CH_3.CO.CH_2.CH_3$
Butanone

$CH_3.CO.CH_2.CH_2.CH_3$
2-Pentanone

$\overset{1}{C}H_3.\overset{2}{C}H(CH_3).\overset{3}{C}O.\overset{4}{C}H_2.\overset{5}{C}H_3$
2-Methyl-3-pentanone

$\overset{1}{C}H_3.\overset{2}{C}O.\overset{3}{C}H(C_2H_5).\overset{4}{C}O.\overset{5}{C}H_2.\overset{6}{C}H_3$
3-Ethyl-2: 4-hexandione

In naming a ketone derived from an *unsaturated* hydrocarbon, the numbering of carbon atoms begins from the **end nearer to the double or the triple bond** (and *not*, to the —CO— group), as in the following case :—



$$\overset{1}{C}H_3.\underset{\displaystyle CH_3}{\overset{2}{C}} = \overset{3}{C}H.\overset{4}{C}H_2.\overset{5}{C}H_2.\overset{6}{C}O.\overset{7}{C}H_3$$

2-Methyl-2-hepten-6-one

2. **Formation of Aldehydes and Ketones.**—Aldehydes and ketones may be obtained by the following methods :—

(1) **From Primary and Secondary Alcohols :—**

(1) *By Oxidation.* When a *primary* alcohol is submitted to oxidation with potassium dichromate and dilute sulphuric acid (or chromic anhydride dissolved in glacial acetic acid), it yields first an aldehyde and then a carboxylic acid ; *e.g.*,

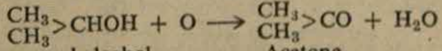
$CH_3.CH_2OH$
Ethyl Alcohol

$CH_3.CHO$
Acetaldehyde

$CH_3.COOH$
Acetic Acid

As the initial product (*i.e.*, the aldehyde) is even more susceptible to oxidation than the starting material (*i.e.*, the alcohol) it must be rapidly separated from the reaction mixture to protect it from further oxidation. This is made possible by the fact that aldehydes are far more volatile than the corresponding alcohols, as will appear from the Table on the next page.

Secondary alcohols on oxidation give ketones,



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CHOH + O \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}CO + H_2O$$

Isopropyl alcohol Acetone

As ketones are more stable to oxidation than aldehydes, they are readily obtained by oxidation and need no precaution for protection from further oxidation.

Comparison of Boiling Points of Alcohols and Aldehydes :—

Alcohols	b.p.	Aldehydes	b.p.
Methyl alcohol	65°C	Formaldehyde	—21°C
Ethyl alcohol	78	Acetaldehyde	21
n-Propyl alcohol	97	Propionaldehyde	49
n-Butyl alcohol	118	*n* Butyraldehyde	75
Isobutyl alcohol	108	Isobutyraldehyde	61

(*ii*) *By Catalytic Dehydrogenation.* When the vapours of primary and secondary alcohols are passed over finely-divided copper (obtained by reducing CuO) at 300°C, we get hydrogen and aldehydes[1] or ketones ; *e.g.*,

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2$$
$$(CH_3)_2CH.OH \longrightarrow (CH_3)_2CO + H_2$$

(*iii*) **Oppenauer Oxidation**[2] (1937). Oppenauer has discovered an elegant method for the oxidation of secondary alcohols to ketones by means of a specific reagent, **aluminium tertiary-butoxide.** The alcohol to be oxidized is refluxed with the reagent together with a large excess of acetone. The net reaction is the dehydrogenation of the alcohol, the *hydrogen passing on to acetone*, which gets reduced to isopropyl alcohol :

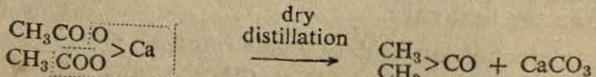
$$R.CH(OH).R' + (CH_3)_2C{=}O \xrightleftharpoons{\text{Al } t\text{-butoxide}} RCOR' + (CH_3)_2CHOH$$

The reaction has the advantage of being *specific to the alcoholic group*, and is therefore particularly useful for oxidizing *unsaturated* secondary alcohols to the corresponding unsaturated ketones, *the double bond remaining unaffected*.

The Oppenauer reaction can also be used for the oxidation of *primary* alcohols (particularly, the unsaturated alcohols) to aldehydes. The acetone, in this case, is replaced by *p*-benzoquinone, which is a better hydrogen acceptor than acetone.

(2) **From Carboxylic Acids by Pyrolysis.—**

(*i*) *By Dry Distillation of Metal Salts.* When the calcium salt of a fatty acid (other than formic) is subjected to dry distillation, a *symmetrical* ketone is obtained. Thus, from calcium acetate we get acetone :



$$\begin{matrix}CH_3CO.O\\CH_3.COO\end{matrix}\!>Ca \xrightarrow{\text{dry distillation}} \begin{matrix}CH_3\\CH_3\end{matrix}\!>CO + CaCO_3$$

---

[1] The term *aldehyde* is an abbreviation of *alcohol dehydrogenatum*, *i.e.*, alcohol from which hydrogen has been removed. It refers to the production of aldehydes from alcohols by loss of hydrogen.

[2] Oppenauer oxidation is the counterpart of the previously discovered Meerwein-Ponndorf reduction (p. 228).

In some cases, improved results can be obtained by the use of barium, manganese and thorium salts.

Calcium formate, when heated alone, yields formaldehyde :

$$(HCOO)_2Ca \longrightarrow HCHO + CaCO_3$$

When a mixture of this salt with the calcium salt of some other fatty acid is used, the latter is reduced to the corresponding aldehyde :—

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

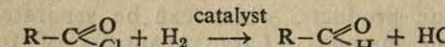
If a mixture of calcium salts of fatty acids (excluding formic) is employed, a mixed ketone is produced in addition to the simple ones :—

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\substack{\text{Calcium}\\\text{propionate}}}{(C_2H_5COO)_2Ca} \longrightarrow \underset{\substack{\text{Methyl ethyl}\\\text{ketone}}}{2CH_3.CO.C_2H_5} + 2CaCO_2$$

(*ii*) *By Direct Pyrolysis.* Instead of preparing the salt as a dry solid before pyrolysis, the acid itself may be distilled and the vapour passed through a heated tube packed with a suitable metal oxide. Thus, in the case of acetic acid, manganous oxide deposited on pumice gives a very good yield of acetone :

$$2CH_3COOH \xrightarrow{MnO,300^\circ} 2CH_3COCH_3 + H_2O + CO_2$$

(3) **Rosenmund Reduction of Acid Chlorides.** An important method of converting a carboxylic acid into the corresponding aldehyde is through the catalytic reduction of its chloride :



$$R-C{\lessdot}^{O}_{Cl} + H_2 \xrightarrow{\text{catalyst}} R-C{\lessdot}^{O}_{H} + HCl$$

The method, due to Rosenmund, is based on the technique of differeniating between the speed of replacement of chlorine by hydrogen and that of hydrogenation of the resulting aldehyde to the alcohol. The conditions are so arranged as to bring about the former reaction with almost entire exclusion of the latter.

The Rosenmund procedure consists in bubbling hydrogen gas through a hot solution of the acid chloride dissolved in toluene or xylene in the presence of a specially prepared catalyst (**palladium impregnated on barium sulphate**) to which a small proportion of a poisoning or deactivating agent containing sulphur (thiourea or thioquinanthrene) has been added to bring down the activity of the catalyst to such an extent that the hydrogenation reaction is effectively eliminated. The exit gas is passed into standard alkali to absorb the evolved HCl and thus to follow the course of the reaction by titration, The temperature is maintained near the lowest point at which HCl is evolved, and, as soon as one equivalent of HCl has been evolved, the passage of hydrogen is stopped.

(4) **From Dihalides.** When a dihalogen derivative of an alkane, containing both the halogen atoms linked to the *same* carbon, is

hydrolysed with superheated water[1], or by boiling with water and plumbous oxide, we get an aldehyde or a ketone, the former, if the two halogen atoms be linked to a *terminal* carbon atom, and the latter, if they be carried by an *intermediate* carbon atom. The reaction is supposed to occur in two stages: The dihydroxy derivative, which is first formed, loses the elements of water, yielding an aldehyde or a ketone :

$$\underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} \xrightarrow{HOH} \underset{\substack{\text{unstable}\\ \text{dihydroxy compound}}}{CH_3.CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

$$\underset{\text{2,2-Dichloropropane}}{CH_3.CCl_2.CH_3} \xrightarrow{HOH} \underset{\substack{\text{unstable}\\ \text{dihydroxy compound}}}{CH_3.C(OH)_2.CH_3} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

(5) **From Hydrocarbons :**

(*i*) *From Alkanes, by Controlled Oxidation.* Combustion of hydrocarbons (even of simple molecules like CH_4 and C_2H_6) to produce carbon dioxide and water does not take place in one step. It proceeds in stages with the intermediate production of partially oxidized molecules (alcohols, aldehydes, ketones and carboxylic acids). Under ordinary conditions of combustion, it is not possible to separate, or even detect these intermediate products ; they get combusted too fast, giving the ultimate products, carbon dioxide and water. Desirable results can be obtained, however, by mixing the hydrocarbon gases with air in suitable proportions and heating the mixture to suitable temperatures. This method of **controlled oxidation** yields a mixture of oxidation products, which can be separated from one another by suitable methods. Large quantities of formaldehyde, acetaldehyde, acetone, methyl alcohol, etc. are now manufactured by this method from natural gas.

(*ii*) *From Alkenes by Ozonolysis.* Refer to page 159.

(*iii*) **From Alkynes.** When acetylene is treated with dilute sulphuric acid in the presence of mercuric sulphate (catalyst), we get acetaldehyde :—

$$\underset{\text{Acetylene}}{HC\equiv CH} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

A homologue of acetylene, on similar treatment, adds on a molecule of water at the triple bond in accordance with Markownikoff's rule and yields a ketone ; *e.g.*,

$$\underset{\text{Propyne}}{CH_3.C\equiv CH} + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

(6) **By Acetoacetic Ester Synthesis.** A very useful method for preparing *ketones* is by the hydrolysis of acetoacetic ester and its derivatives with alkalis (see chapter 26, sec. 4).

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[1] Alkali cannot be used for hydrolysis in this case, as it would resinify the resulting aldehyde.

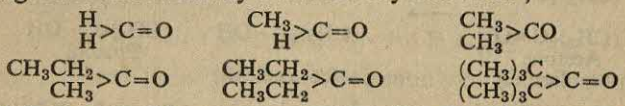
(7) **From Grignard Reagents.** When a Grignard reagent is treated with ethyl orthoformate and the product hydrolysed, we get an aldehyde (p. 217). Similarly, treatment with an amide gives a ketone (p. 219).

3. Physical Properties of Aldehydes and Ketones.—Excluding formaldehyde, which, at ordinary temperatures, is a gas, the aldehydes and ketones up to about C_{11} are colourless, mobile liquids, the higher members being solids. As a rule, aldehydes possess an unpleasant pungent odour, while ketones have a pleasant smell The first two or three members of both the homologous series are readily soluble in water, but as the molecular weight rises, the solubility rapidly decreases, the higher members being practically insoluble in water They are, however, readily soluble in alcohol and ether. The specific gravity and the boiling points continuously rise with the increase in the number of carbon atoms.

4. Reactions of Carbonyl Group.—The characteristic group present in aldehydes and ketones is the carbonyl group, $>C=O$. The double bond of this group, like the ethylenic double bond, represents a state of unsaturation. Hence, aldehydes and ketones undergo addition reactions with a number of substances.

Dependence of Reactivity of Carbonyl Group on size of attached Alkyl Groups.—

The reactivity of the carbonyl group depends on the size of the alkyl groups with which it is linked. The smaller the alkyl group, the greater is the reactivity of the carbonyl group. Thus, in the following cases the reactivity continuously decreases ;



$$\substack{H\\H}>C=O \qquad \substack{CH_3\\H}>C=O \qquad \substack{CH_3\\CH_3}>CO$$

$$\substack{CH_3CH_2\\CH_3}>C=O \qquad \substack{CH_3CH_2\\CH_3CH_2}>C=O \qquad \substack{(CH_3)_3C\\(CH_3)_3C}>C=O$$

formaldehyde being the most and ditertiary butyl ketone the least reactive.

The reason for the decrease of reactivity with the size of the attached alkyl group is supposed to be the **spatial effect**, *i.e.*, the protective action of the alkyl groups on the carbonyl group. The larger the alkyl group, the greater will be the protection that it affords to the carbonyl group from the attacking molecules of a reagent.

Direction of Carbonyl Addition Reactions.—

The direction of the carbonyl addition reactions is determined by the fact that oxygen atom is much more electronegative (electronphilic) than the carbon atom. Hence, electron displacement occurs within the carbonyl group with the result that a fractional negative charge is acquired by the oxygen atom and a fractional positive charge by the carbon atom, as shown in the margin. Hence, *the more electropositive atom or group from the reacting molecule undergoing addition with an aldehyde or ketone unites with the oxygen atom of the carbonyl*

$$>\underset{+\delta}{C}=\underset{-\delta}{O}$$

group and the more electronegative one unites with the carbon atom. This is the underlying principle of the addition reactions of aldehydes and ketones given below. We shall discuss the reactions of the carbonyl group under three separate heads :—

(1) **Addition Reactions.**—

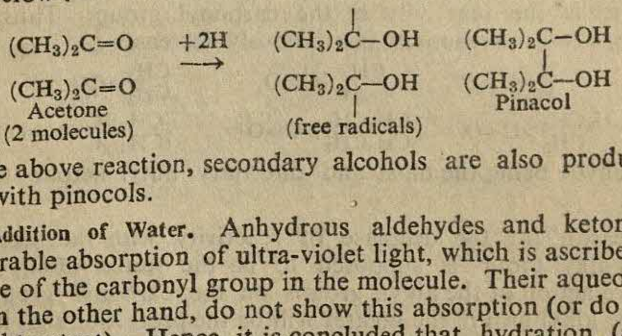
(*i*) **Addition of Hydrogen.** Strong reducing agents (*e.g.*, sodium amalgam and dilute sulphuric acid) bring about hydrogenation of aldehydes and ketones with the production of primary alcohols in the case of the former and secondary alcohols in that of the latter :—

$$\underset{\text{Acetaldehyde}}{CH_3.C\lessgtr^{H}_{O}} + 2H \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2H \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3}$$

Various reagents for bringing about reduction of aldehydes and ketones to alcohols are given on page 227 (*q.v.*).

Binomolecular Reduction. *Pinacol Formation.* When *ketones* (not aldehydes) are carefully treated with sodium, sodium amalgam or magnesium amalgam, in *strongly alkaline* solution, *two* molecules simultaneously react, each taking up only *one* atom of hydrogen, and the unsaturated residues (or free radicals) thus produced combine with each other. The products are dihydric ditertiary alcohols, called **Pinacols.** The course of the reaction in the case of acetone is shown below :—



$$\begin{array}{ccccc} (CH_3)_2C{=}O & & (CH_3)_2\overset{|}{C}{-}OH & & (CH_3)_2C{-}OH \\ & \xrightarrow{+2H} & & & | \\ (CH_3)_2C{=}O & & (CH_3)_2\underset{|}{C}{-}OH & & (CH_3)_2C{-}OH \\ \text{Acetone} & & & & \text{Pinacol} \\ \text{(2 molecules)} & & \text{(free radicals)} & & \end{array}$$

In the above reaction, secondary alcohols are also produced together with pinocols.

(*ii*) **Addition of Water.** Anhydrous aldehydes and ketones show considerable absorption of ultra-violet light, which is ascribed to the presence of the carbonyl group in the molecule. Their aqueous soluions, on the other hand, do not show this absorption (or do so only to a slight extent). Hence, it is concluded that hydration (addition of water) of carbonyl group has occurred with the production of the unstable compounds called **orthoaldehydes and orthoketones** :—

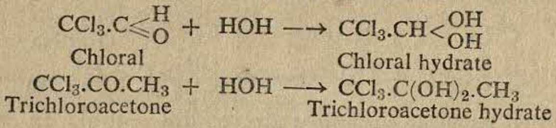
$$^{R}_{Y}{>}C{=}O + H_2O \rightleftharpoons \underset{\substack{\text{(Orthoaldehyde}\\ \text{or orthoketone)}^1}}{^{R}_{Y}{>}C{<}^{OH}_{OH}}$$

Orthoaldehydes and orthoketones are too unstable to exist as such, as, in accordance with the general rule, they immediately lose water between the two hydroxyls linked to the same carbon atom with

---

[1] **The symbol, Y, used in the equation represents H in the case of an aldehyde and an alkyl group in the case of a ketone.**

regeneration of the aldehyde or the ketone. A few compounds of this type, for example *chloral hydrate* (p. 288) and (*trichloroacetone hydrate*), however, are stable enough to be isolated.



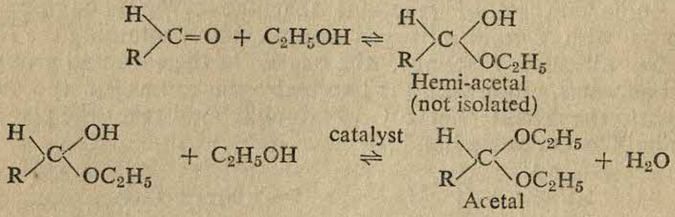
$$CCl_3.C{\leqslant}^{H}_{O} + HOH \longrightarrow CCl_3.CH{<}^{OH}_{OH}$$

Chloral — Chloral hydrate

$$CCl_3.CO.CH_3 + HOH \longrightarrow CCl_3.C(OH)_2.CH_3$$

Trichloroacetone — Trichloroacetone hydrate

(*iii*) **Reaction with alcohols.** When an aldehyde is warmed with an alcohol (anhydrous) in the presence of a little HCl or anhydrous copper sulphate, there occurs a reaction which is supposed to be taking place in two steps. A molecule of the alcohol first adds on at the carbonyl group, and the product then immediately reacts with a second molecule of the alcohol. The final product is called an **acetal** and the intermediate product a **hemi-acetal.**

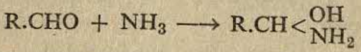


Hemi-acetal (not isolated)

Acetal

Ketones, on similar treatment, give **ketals**, but the yields are very poor.

(*iv*) **Addition of ammonia.** The *primary* action between an aldehyde and ammonia is addition :—



$$R.CHO + NH_3 \longrightarrow R.CH{<}^{OH}_{NH_2}$$

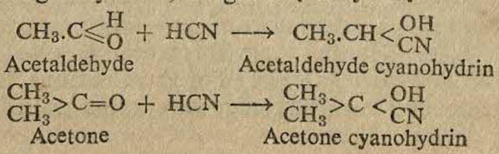
The products are **alpha-amino alcohols** commonly called **aldehyde ammonias.**

The aldehyde ammonias, however, are stable in very few cases. A notable example is **trichloroacetaldehyde ammonia,** $CCl_3.CH(OH)NH_2$, which exists as such. The simpler aldehyde ammonias (*e.g.*, that of acetaldehyde) undergo polymerization to form **trimeric products.**

The aldehyde ammonias (both the simple ones and the trimers) are decomposed by dilute acids, regenerating the original aldehyde. For this reason, they are often used for the **purification of aldehydes.**

The reactions between ammonia and aldehydes, however, are not uniform. Thus formaldehyde gives hexamethylenetetramine (p. 284); benzaldehyde produces hydrobenzamide.

(*v*) **Addition of hydrogen cyanide.** When an aldehyde or a ketone is treated with hydrogen cyanide, we get a **cyanohydrin :**



$$CH_3.C{\leqslant}^{H}_{O} + HCN \longrightarrow CH_3.CH{<}^{OH}_{CN}$$

Acetaldehyde — Acetaldehyde cyanohydrin

$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C=O + HCN \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}^{OH}_{CN}$$

Acetone — Acetone cyanohydrin

group and the more electronegative one unites with the carbon atom. This is the underlying principle of the addition reactions of aldehydes and ketones given below. We shall discuss the reactions of the carbonyl group under three separate heads :—

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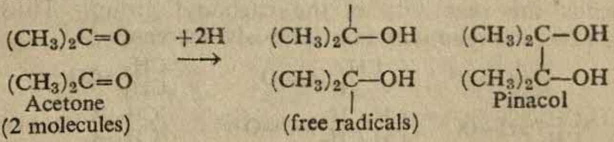

$$\underset{\substack{\text{Acetone}\\\text{(2 molecules)}}}{\begin{matrix}(CH_3)_2C{=}O\\(CH_3)_2C{=}O\end{matrix}} \xrightarrow{+2H} \underset{\text{(free radicals)}}{\begin{matrix}(CH_3)_2\overset{|}{C}{-}OH\\(CH_3)_2\underset{|}{C}{-}OH\end{matrix}} \quad \underset{\text{Pinacol}}{\begin{matrix}(CH_3)_2C{-}OH\\|\\(CH_3)_2C{-}OH\end{matrix}}$$

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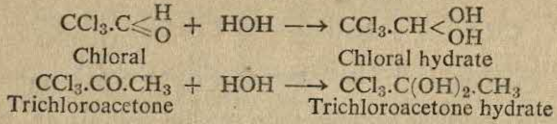

$$\underset{\text{Chloral}}{CCl_3.C{\lessgtr}^{H}_{O}} + HOH \longrightarrow \underset{\text{Chloral hydrate}}{CCl_3.CH{<}^{OH}_{OH}}$$

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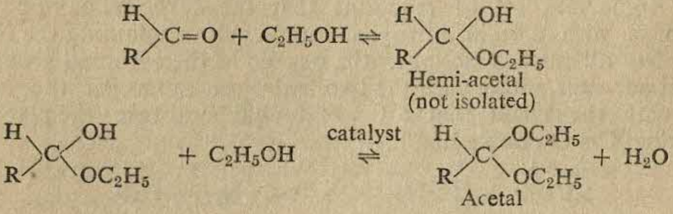

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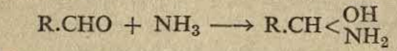

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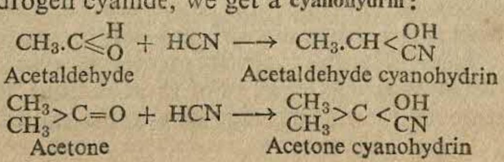
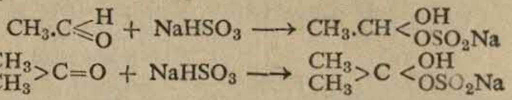


$$\underset{\text{Acetaldehyde}}{CH_3.C{\lessgtr}^{H}_{O}} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_3.CH{<}^{OH}_{CN}}$$

$$\underset{\text{Acetone}}{{}^{CH_3}_{CH_3}{>}C{=}O} + HCN \longrightarrow \underset{\text{Acetone cyanohydrin}}{{}^{CH_3}_{CH_3}{>}C{<}^{OH}_{CN}}$$

(*vi*) **Addition of sodium bisulphite.** On shaking aldehydes or ketones with very concentrated solutions of sodium bisulphite, crystalline addition compounds are obtained :



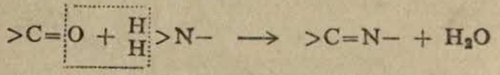
$$CH_3.C{\lessgtr}\substack{H\\O} + NaHSO_3 \longrightarrow CH_3.CH{<}\substack{OH\\OSO_2Na}$$

$$\substack{CH_3\\CH_3}{>}C{=}O + NaHSO_3 \longrightarrow \substack{CH_3\\CH_3}{>}C{<}\substack{OH\\OSO_2Na}$$

These so-called **bisulphite compounds** are readily soluble in water, but are insoluble in very concentrated solutions of $NaHSO_3$. On warming them with dilute acids or alkalis, the aldehyde or ketone is again set free. Hence the formation of these compounds is employed for the **purification** and **separation** of an aldehyde or a ketone.

(*vii*) **Addition of Grignard's reagents.** (See page 218).

(2) **Conversion of carbon-oxygen double bond to carbon-nitrogen double bond.** A very important set of reactions that the carbonyl compounds undergo is with certain nitrogen compounds containing the NH_2 group. In all such reactions, the oxygen of the carbonyl group is removed as water, along with the two hydrogen atoms of the NH_2 group with the result that a C=N double bond takes the place of the original C=O double bond :—

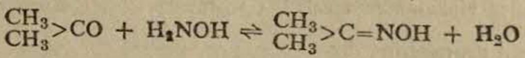


$$>C{=}\boxed{O + \substack{H\\H}}{>}N- \longrightarrow >C{=}N- + H_2O$$

Three most important reagents of this class from the practical point of view are :—

(*i*) **Hydroxylamine,** NH_2OH, which produces **oximes** :—

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2NOH \rightleftharpoons \underset{\substack{\text{Acetaldoxime}\\\text{(an aldoxime)}}}{CH_3\,CH{=}NOH} + H_2O$$



$$\substack{CH_3\\CH_3}{>}CO + H_2NOH \rightleftharpoons \substack{CH_3\\CH_3}{>}C{=}NOH + H_2O$$

Acetone   Acetone oxime
(a ketoxime)

(*ii*) **Phenylhydrazine,** $H_2N.NH.C_6H_5$, which produces **phenylhydrazones :**

$$CH_3.CHO + H_2N.NH.C_6H_5 \rightleftharpoons \underset{\text{Acetaldehyde phenylhydrazone}}{CH_3.CH{=}N.NH.C_6H_5} + H_2O$$

(*iii*) **Semicarbazide,** $H_2N.NH.CO.NH_2$, which produces **semicarbazones:**

$$(CH_3)_2CO + H_2N.NH.CO.NH_2 \rightleftharpoons \underset{\text{Acetone semicarbazone}}{(CH_3)_2C{=}N.NH.CO.NH_2} + H_2O$$

Oximes, phenylhydrazones and semicarbazones are very readily crystallizable and possess sharp melting points. Hence, the formation of these derivatives is employed for the **identification of individual aldehydes and ketones.** Further, the aldehydes and ketones can be easily regenerated by treatment of any of these derivatives with hydrochloric acid. Hence, their formation is also utilized for the *isolation of aldehydes and ketones.* For these reasons, hydroxylamine, phenylhydrazine and semicarbazide are often called **carbonyl-group reagents.**

(3) **Replacement of carbonylic oxygen by other elements.** We may here give two reactions of aldehydes and ketones involving replacement of carbonylic oxygen by other elements. In one of these the oxygen atom gets replaced by two chlorine atoms and in the other by two hydrogen atoms :—

(*i*) **Action of phosphorus pentachloride.** This reagent replaces the carbonylic oxygen by two chlorine atoms,

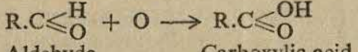
$$RCHO + PCl_5 \longrightarrow RCHCl_2 + POCl_3,$$
$$R_2CO + PCl_5 \longrightarrow R_2CCl_2 + POCl_3,$$

and thus serves to differentiate aldehydes and ketones from alcohols and ethers in so far as the relative *constitutions* of these three classes of oxygen-containing carbon compounds is concerned. As already mentioned, in the case of alcohols this reagent replaces the OH group by a chlorine atom, while in ethers it splits the molecule at the oxygen atom.

(*ii*) **Clemmensen reduction.** When a ketone (or an aromatic aldehyde) is heated with amalgamated zinc and concentrated hydrochloric acid, the oxygen of the carbonyl group is replaced by two hydrogen atoms, with the production of a *hydrocarbon.* The reaction is of importance in preparing pure samples of hydrocarbons (especially aromatic hydrocarbons and cyclanes).

$$\underset{\text{Acetophenone}}{C_6H_5.CO.CH_3} + 4H \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.CH_2.CH_3} + H_2O$$

5. Reducing Action of Aldehydes.—*Oxidation of the —CHO to the —COOH Group.* The hydrogen atom directly linked to the carbonyl group confers **active reducing properties** on the aldehyde molecule. By virtue of this, aldehydes reduce even such mild oxidizing agents as **ammoniacal silver nitrate** and the **Fehling solution** (an alkaline solution of cupric sulphate in the presence of Rochelle salt). These reagents are *specific* for aldehydes and do not attack alcohols or the ethylenic compounds. Reduction of these reagents, therefore, is a **characteristic test of aldehydes.** The aldehyde group takes up an atom of oxygen and changes to the carboxyl group :—



$$R.C\lesssim^{H}_{O} + O \longrightarrow R.C\lesssim^{OH}_{O}$$

Aldehyde Carboxylic acid

So, an aldehyde, on treatment with mild oxidizing agents, gives a *carboxylic acid containing the same number af carbon atoms as the aldehyde* itself.

Tests of Aldehydes.—

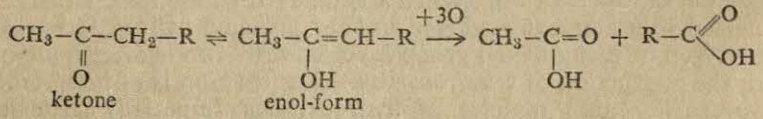
Expt. 1. To a solution of silver nitrate add, drop by drop, a very dilute solution of ammonia, until the precipitate of silver hydroxide, first formed *just* redissolves. Add a few drops of acetaldehyde and place the test-tube in boiling-hot water. A bright silver mirror will be formed on the inside of the test-tube.

Expt. 2. Add a dilute solution of acetaldehyde to a few ml. of Tollens reagent. A silver mirror is deposited in the cold.

Tollens' reagent is prepared by mixing together equal volumes of 10 per cent aqueous solutions of silver nitrate and sodium hydroxide, and adding just enough ammonia to dissolve the silver hydroxide.

Expt. 3. Add a few drops of acetaldehyde to some Fehling's solution (a solution of cupric sulphate containing Rochelle salt and caustic soda), and warm the mixture. A red precipitate of cuprous oxide will be formed.

6. Behaviour of Ketones on Oxidation.—Ketones, since they do not contain a readily oxidizable hydrogen atom, possess no reducing properties, and do not react with such mild oxidizing agents as the ammoniacal silver nitrate or the Fehling solution. When submitted to vigorous oxidation (*e.g.*, treatment with hot, concentrated nitric acid or refluxing with chromic acid), the ketone molecule breaks up, giving a mixture of acids having *smaller* number of carbon atoms. The **oxidative breakdown of the ketone molecule occurs through the enolic form** present in equilibrium. The molecule of the enol form breaks at the double bond ; *three atoms of oxygen* are added on, with the **production of two carboxyl groups** as shown below :—



$$\underset{\text{ketone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_2-R} \rightleftharpoons \underset{\text{enol-form}}{CH_3-\underset{\underset{OH}{|}}{C}=CH-R} \xrightarrow{+3O} CH_3-\underset{\underset{OH}{|}}{C}=O + R-C\begin{array}{l}\nearrow O\\ \searrow OH\end{array}$$

The **oxidative breakdown of unsymmetrical ketones** occurs in accordance with the following *two rules* :—

(1) Of the two carbon atoms adjacent to the carbonyl group, the one carrying a *smaller number of hydrogen atoms* is oxidized, as in the above case.

(2) If both these carbon atoms hold the same number of hydrogens, then the *smaller* of the two radicals is oxidized ; *e.g.*,

$$CH_3.CH_2.CO.CH_2.CH_2.CH_3 \longrightarrow CH_3.COOH + CH_3.CH_2.CH_2.COOH$$

The oxidizing action of **selenium dioxide**, SeO_2, on aldehydes and ketones is remarkable. This reagent always **converts a CH_2 group in the alpha position into the carbonyl group.** Thus, acetone gives pyruvic aldehyde and methyl ethyl ketone gives diacetyl :—

$$CH_3.CO.CH_3 + SeO_2 \longrightarrow \underset{\text{Pyruvic aldehyde}}{CH_3.CO.CHO} + H_2O + Se$$

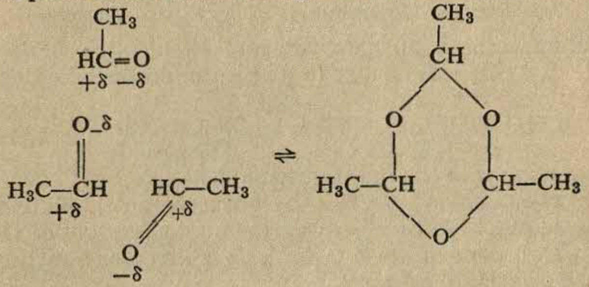
$$CH_3.CO.CH_2.CH_3 + SeO_2 \longrightarrow \underset{\text{Diacetyl}}{CH_3.CO.CO.CH_3} + H_2O + Se$$

7. Polymerization of Aldehydes : *Union of Molecules through Carbon-Oxygen Links.* The lower aldehydes resemble alkenes in polymerizing readily. The following are some important examples :—

(1) **Paraldehyde.** When acetaldehyde (b.p. 21°), contained in a beaker, is touched with a glass rod moistened with concentrated sulphuric acid, a violent ebullition occurs and the liquid undergoes a marked contraction in volume. The resulting liquid, called "paraldehyde", boils at 124° and has been shown to be a trimer of acetaldehyde :—

$$\begin{array}{ccc} 3CH_3.CHO & \overset{H_2SO_4}{\rightleftharpoons} & (CH_3.CHO)_3 \\ \text{Acetaldehyde} & & \text{Paraldehyde} \\ \text{(b.p. 21°)} & & \text{(b.p. 124°)} \\ \text{(miscible with water)} & & \text{(immiscible with water)} \end{array}$$

The reaction is reversible, and an equilibrium is established when the conversion is about 95 per cent complete. Since paraldehyde is stable towards oxidizing agents and shows none of the addition reactions characteristic of the carbonyl group, the linking together of the aldehyde molecules must have occurred through the —C—O— groups. So paraldehyde molecule is regarded as having a six-membered carbon-oxygen ring. The reaction is best explained by assuming the union to have taken place by addition at the positive and negative poles of the three aldehyde molecules.



The conversion of acetaldehyde into paraldehyde and *vice versa* is very easy, as the former is volatile and soluble in water, whereas the latter has a much higher boiling point and is immiscible with water. Hence, to prepare paraldehyde from acetaldehyde, the latter is treated with a few drops of concentrated sulphuric acid. The product is washed with water to dissolve out the catalyst and the small amount of unchanged acetaldehyde. The paraldehyde, thus separated, is dried and distilled.

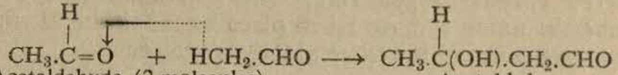
In the absence of an acid catalyst, the trimer is quite stable. It is inert, non-volatile and not subject to oxidation. Hence, it is a very convenient form in which acetaldehyde may be potentially stored. To convert paraldehyde back into acetaldehyde, a little sulphuric acid is added and acetaldehyde distilled off. Progressive shifting of the equilibrium to the left results in complete regeneration of the monomer.

(2) **Metaldehyde.** When acetaldehyde is treated with such acid catalysts as HCl, SO_2, $ZnCl_2$, etc., at a temperature of 0°, or lower, it gives rise to a crystalline tetramer, $(CH_3CHO)_4$, called "Metaldehyde". When heated beyond 100°, metaldehyde undergoes depolymerization. Like paraldehyde, it is devoid of all aldehydic properties, and is assigned a similar structure. The ring in this case consists of *eight* atoms (*viz.*, 4 carbons and 4 oxygens) instead of six in paraldehyde. Metaldehyde can be reconverted into acetaldehyde by distillation with dilute acid.

Metaldehyde burns with a non-luminous flame, and is employed as a solid fuel for household use under the name "Meta".

(3) *Trioxane* and *Paraformaldehyde* are the two well-known polymers of formaldehyde (sec. 7).

8. Aldol Condensation.—*Union of Molecules through Carbon-carbon Links.* When an aldehyde having a hydrogen atom in the *alpha*-position is treated with small amounts of alkalis (alkali bicarbonate, carbonate, acetate, alcoholates or dilute alkali hydroxides), it undergoes aldol condensation. The reaction involves—(*i*) the **carbonylic oxygen** of one aldehyde molecule, and (*ii*) an **alpha hydrogen atom** in a second molecule of the aldehyde, *i.e.*, the hydrogen attached to carbon in the *alpha*-position to the carbonyl group. This hydrogen atom migrates to carbonylic oxygen of the first aldehyde molecule, and a *carbon-to-carbon* link is established between the two molecules as shown below in the case of acetaldehyde :—



$$\overset{H}{CH_3.C{=}O} + HCH_2.CHO \longrightarrow CH_3.\overset{H}{C}(OH).CH_2.CHO$$

Acetaldehyde (2 molecules) Acetaldol

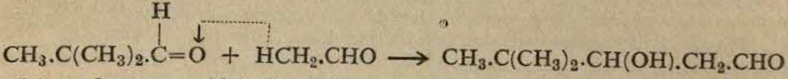
The product is both an aldehyde and an alcohol, hence the name "*aldol*." It easily loses water to give an unsaturated aldehyde ; *e.g.*,

$$\underset{\text{Acetaldol}}{CH_3.CH(OH).CH_2.CHO} \xrightarrow{-H_2O} \underset{\text{Crotonaldehyde}}{CH_3CH{=}CH.CHO}$$

The conversion into the unsaturated aldehyde occurs even during the course of the reaction. In fact, by proper control of conditions, the unsaturated aldehyde can be made the major product of the reaction. Hence, aldol condensation affords a convenient method for the **synthesis of unsaturated aldehydes.**

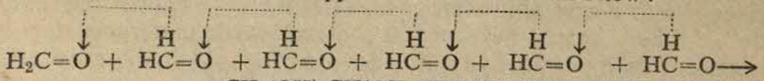
Of course, aldol condensation can only occur with those aldehydes which have at least one atom of hydrogen on the carbon atom in the *alpha*-position to the aldehyde group. Hence, an aldehyde of the type $R.C(CH_3)_2.CHO$ cannot undergo aldol condensation.

Aldol condensation can also occur with aldehydes of different structure. provided at least one of these fulfils the requisite condition of having an alpha hydrogen in the molecule. Thus,



$$CH_3.C(CH_3)_2.\overset{H}{C}{=}O + HCH_2.CHO \longrightarrow CH_3.C(CH_3)_2.CH(OH).CH_2.CHO$$

More than two aldehyde molecules may undergo aldol condensation. An important example is that of formaldehyde, which in contact with lime (or baryta water) yields a sweet, syrupy liquid containing hexoses among other things. Here a chain of aldol condensations is supposed to occur as shown below :

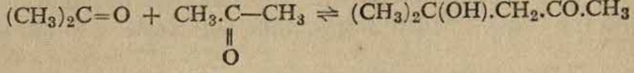


$$H_2C{=}O + \overset{H}{HC{=}O} + \overset{H}{HC{=}O} + \overset{H}{HC{=}O} + \overset{H}{HC{=}O} + \overset{H}{HC{=}O} \longrightarrow$$

$$\underset{\text{an aldohexose}}{CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO}$$

Resinification of Aldehydes. All aldehydes that undergo aldol condensation give **resins** (brown, sticky, water-insoluble materials) when warmed with concentrated alkali solutions. These are supposed to be produced by repeated aldol condensations until a very large molecule has been produced. Resinification of aldehydes by alkalis is a **useful test** for aldehydes having an alpha hydrogen atom in the molecule.

Aldol Condensation of Ketones. Condensation of the aldol type is not so common in ketones. Yet, it does occur in certain cases. Thus, acetone, when treated with barium hydroxide, gives **diacetone alcohol** :—



$$(CH_3)_2C{=}O + CH_3.\underset{\underset{O}{\|}}{C}{-}CH_3 \rightleftharpoons (CH_3)_2C(OH).CH_2.CO.CH_3$$

9. Cannizzaro's Reaction (1853).—Aldehydes having no hydrogen atom in the *alpha*-position, when treated with a concentrated alkali solution (50% NaOH or KOH aqueous or alcoholic solution), undergo disproportionation (compensated oxidation-reduction reaction), in which one molecule of the aldehyde gets oxidized to the carboxylic acid at the expense of another, which is reduced to the corresponding primary alcohol. Thus, formaldehyde, H.CHO and trimethylacetaldehyde react as under :

$$2HCHO + KOH \longrightarrow \underset{\text{Potassium formate}}{HCOOK} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$(CH_3)_3C.CHO + KOH \longrightarrow (CH_3)_3C.COOK + (CH_3)_3C.CH_2OH$$

This reaction was discovered by the Italian chemist Stanislao Cannizzaro in 1853, and is therefore known as '*Cannizaro reaction*'. In the case of aliphatic aldehydes, the Cannizzaro reaction is of rare occurrence, as most of them possess an activated hydrogen atom in the *alpha*-position and, for that reason, undergo the more rapid aldol condensation. Among the aromatic aldehydes the reaction is far more common (*see* under Benzaldehyde).

Crossed Cannizzaro Reaction.—The Cannizzaro reaction can occur between two different aldehydes, and, in that case, is called a "crossed" Cannizzaro reaction. Thus benzaldehyde and formaldehyde react to produce benzyl alcohol and potassium formate,

$$C_6H_5CHO + HCHO + NaOH \rightarrow C_6H_5CH_2OH + HCOONa$$

10. Tischenko Reaction (1906).—All aldehydes, whether possessing an active hydrogen atom in the *alpha*-position or not, when treated with *aluminium* ethoxide[1], give the ester derived from the corresponding alcohol and the carboxylic acid. Thus, acetaldehyde yields ethyl acetate,

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$$

Child and Adkins (1923-25) have studied the reaction with acetaldehyde, butyraldehyde, *n*-heptaldehyde, benzaldehyde and furfural. In these cases, yields as high as 90 to 95 per cent ester were obtained.

11. Condensation of Ketones with Elimination of Water.—Though, as already described, some ketones undergo aldol condensation, their chief mode of condensation is by the removal of water between the oxygen atom of the carbonyl group of one molecule and two hydrogen atoms on an alpha carbon of another molecule. Thus, acetone, when treated with dehydrating agents, yields the following three products, the first two being obtained by saturating acetone with dry hydrogen chloride and keeping the solution for some time, and the third, by distilling acetone with concentrated sulphuric acid :

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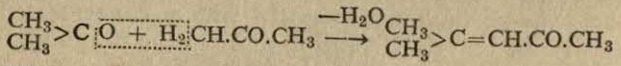
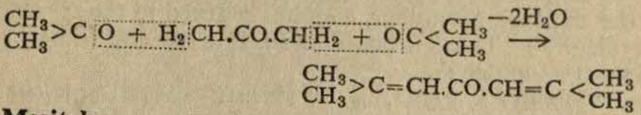
[1] Aluminium butoxide and isobutoxide are even better activators for the Tischenko reaction.

(1) **Mesityl Oxide** :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C\boxed{O + H_2}CH.CO.CH_3 \xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH.CO.CH_3$$

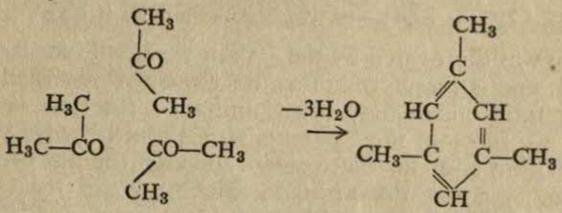
(2) **Phorone** :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C\boxed{O + H_2}CH.CO.CH\boxed{H_2 + O}C<\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{-2H_2O}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH.CO.CH{=}C<\begin{matrix}CH_3\\CH_3\end{matrix}$$

(3) **Mesitylene** :



12. Condensations involving Aldehydes and Ketones with Production of Unsaturated Compounds.

—Aldehydes and ketones undergo condensations with *molecules having an active hydrogen atom in the alpha-position* with respect to the functional group of the reacting molecule. The following are some well-known examples of reactions belonging to this category.

(1) **Claisen Reaction.** This reaction, also called *Claisen-Schmidt Reaction*, involves condensation between an *aromatic* aldehyde (or ketone) with an aldehyde, ketone or ester having an active hydrogen atom in the alpha position, and occurs in the *presence of dilute alkali.* The product is an alpha-beta unsaturated compound. Thus, benzaldehyde and acetaldehyde condense to give cinnamic aldehyde,

$$\underset{\text{Benzaldehyde}}{C_6H_5CH\boxed{O\ +}}\underset{\text{Acetaldehyde}}{\boxed{H_2}CH.CHO} \xrightarrow{NaOH} \underset{\text{Cinnamic aldehyde}}{C_6H_5CH{=}CHCHO} + H_2O$$

(2) **Perkin's Reaction.** This reaction consists in condensing an *aromatic* aldehyde with sodium salt of a fatty acid, in the presence of acetic anhydride, and results in the formation of an aromatic unsaturated acid. Perkin's synthesis is of general application, and is discussed under "Preparation of Cinnamic Acid".

(3) **Knoevenagel Reaction.** This reaction involves a condensation between an aldehyde and a compound having an *active methylene group* in the presence of an organic base (pyridine). It is of particular importance for the preparation of alpha-beta-unsaturated acids (*see* chap. 18, sec. 17).

13. Detection and Identification of Aldehydes and Ketones.—Aldehydes are colourless, neutral substances. If on shaking a little of the substance with fresh, saturated solution of **sodium bisulphite**, a crystalline precipitate is formed, it shows the presence of an aldehyde or a ketone. A more sensitive test is with **2,4-dinitrophenylhydrazine**, which produces coloured, insoluble precipitates with all aldehydes and ketones. Aldehydes are differentiated from ketones by means of : (*i*) **Schiff's Reagent**, and (*ii*) **Tollen's Reagent** (*see* Expt. 2).

Schiff's Reaction. Schiff's reagent is prepared by passing sulphur dioxide into an aqueous solution of **pararosaniline**, until red colour of the dye is discharged (or nearly so). On adding an aldehyde, a pink, red or purple colour will develop *immediately*. After some time, the liquid again turns colourless, owing to the decomposition of the coloured compound produced in the test. Ketones do not produce any immediate colour with Schiff's reagent.

Most aldehydes also reduce **Fehling's solution** (Expt. 3). Benzaldehyde is an exception.

If the substance does not give the above tests, it is tested with a few drops of 10 per cent aqueous solution of **m-phenylenediamine.** A bright green fluorescence proves the presence of a ketone. (Aldehydes also give this test; hence the necessity of performing it after the foregoing tests have been shown to be negative.)

Final identification is based on the **melting point determination of derivatives**—phenylhydrazones, (or 2,4-dinitro-phenylhydrazones), oximes or semicarbazones, (for the preparation of which, see sec. 4).

14. Polymerization and Condensation.—

(1) **Polymerization.** The term "polymerization," in its *general* sense, is applied to any reaction involving the direct union of two or more molecules of a substance to form a new compound whose molecular weight is a multiple of that of the original substance. Thus acetylene, when passed through a red-hot tube, polymerizes to benzene :

$$3C_2H_2 \longrightarrow C_6H_6$$

In the restricted sense in which the term "polymerization" is applied in organic chemistry, it refers to the union of two or more molecules of a substance to form a new compound *capable of conversion into the original substance*. Conversion of acetaldehyde into paracetaldehyde (p. 276) and of formaldehyde into paraformaldehyde and trioxane (p. 283) are typical examples of polymerization.

(2) **Condensation.** This term is applied to the union of molecules, or parts of the same molecule, through *carbon bonds* (or *carbon-nitrogen bonds*) with the production of a substance from which the original compound (or compounds) cannot, as a rule, be regenerated by a simple reaction. Condensation may occur : (*i*) between molecules of the same substance or of different substances (**intermolecular condensation**), or (*ii*) between the parts of the same molecule (**intramole-**

cular condensation). It may or may not be accompanied by loss of component elements. Some important examples of intermolecular condensation are:

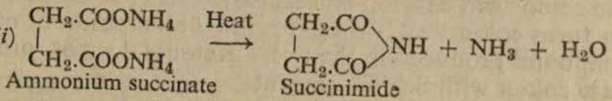
(*i*) Conversion of acetylene into benzene (p. 176).

(*ii*) Condensation of aldehydes and ketones with hydroxylamine, phenylhydrazine and semicarbazide (p. 274).

(*iii*) Aldol condensation (p. 278);

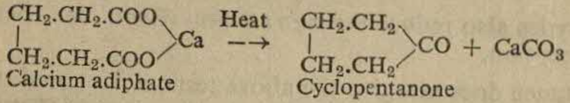
(*iv*) Conversion of acetone to mesityl oxide, phorone, and mesitylene (p. 280).

Examples of intermolecular condensation are :

(*i*)


$$\begin{array}{l} CH_2.COONH_4 \\ | \\ CH_2.COONH_4 \end{array} \xrightarrow{\text{Heat}} \begin{array}{l} CH_2.CO \\ | \\ CH_2.CO \end{array}\!\!\!>NH + NH_3 + H_2O$$

Ammonium succinate — Succinimide

(*ii*)


$$\begin{array}{l} CH_2.CH_2.COO \\ | \\ CH_2.CH_2.COO \end{array}\!\!\!>Ca \xrightarrow{\text{Heat}} \begin{array}{l} CH_2.CH_2 \\ | \\ CH_2.CH_2 \end{array}\!\!\!>CO + CaCO_3$$

Calcium adiphate — Cyclopentanone

15. Formaldehyde, *Methanal*, HCHO.—

Laboratory Preparation. Formaldehyde may be obtained in the laboratory by the oxidation of methyl alcohol. A mixture of methyl alcohol vapour and air is passed over heated spiral of platinum or copper (Fig. 1).

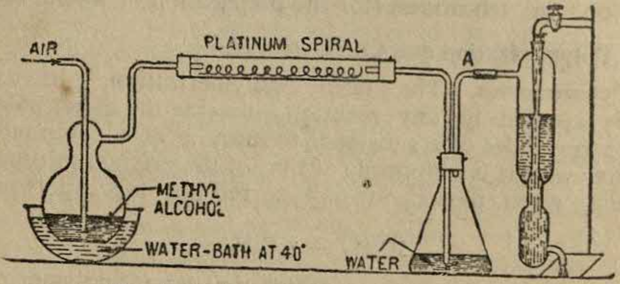


Fig. 1. Preparation of Formaldehyde.

The heat of the reaction raises the temperature of the spiral to redness, and keeps it there, provided the rate at which the gaseous mixture is passed is sufficiently quick. The resulting formaldehyde (which is a gas at the ordinary temperature) is absorbed in water.

Expt. 7. Arrange the apparatus as shown in Fig. 1. Heat methyl alcohol by means of hot water at 40°, placed in a dish, and pass a rapid current of air by attaching the bent tube *A* to a water pump. Heat the hard-glass tube containing the platinum spiral[1], until the latter is red-hot. Formaldehyde is obtained as an aqueous solution.

---

[1] Platinized asbestos or a piece of copper gauze rolled into a spiral, about 2 inches long, may be used instead of a platinum spiral.

Manufacture of Formaldehyde. There are two processes in use for the manufacture of formaldehyde :—

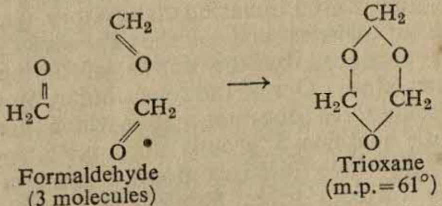
(1) **From Methanol.** In this process, a mixture of superheated methanol vapour and carefully purified air is admitted into a converter, consisting of a water-jacketed vessel of stainless steel containing several layers of **silver-gauze catalyst**. The product, containing about 25 per cent formaldehyde, is fractionated, the methanol being reused in the process. The formaldehyde is dissolved in water to form a 37 per cent solution, called "**Formalin**".

(2) **From Natural Gas or Methane.** Formaldehyde is also manufactured competitively by the controlled oxidation of natural gas or methane.

Physical Properties. Formaldehyde is a gas with a very pungent odour. When cooled with a mixture of solid carbon dioxide and ether, it yields a liquid boiling at 20°. It is soluble in water, alcohol and ether.

Reactions. Formaldehyde, like other aldehydes, gives addition products with hydrogen, hydrogen cyanide, sodium bisulphite and Grignard's reagents. It also reacts with phosphorus pentachloride, hydroxylamine, and phenylhydrazine, and is an active reducing agent.

Formaldehyde has a remarkable tendency to polymerize. When distilled from a 60 per cent aqueous solution containing 2 per cent sulphuric acid, it yields a crystalline trimer called *α*-**trioxymethylene** or **trioxane** :



The trimer, on being heated, regenerates formaldehyde and therefore constitutes a convenient source of gaseous formaldehyde when required for synthetic purposes.

When an aqueous solution of formaldehyde is evaporated, we get "**Paraformaldehyde**", which is a solid mixture of chain polymers containing 100 or more formaldehyde units. These are water-insoluble, amorphous solids called **polyoxymethylenes**. As in the case of trioxane, polyoxymethylenes give formaldehyde on heating.

Formaldehyde **differs** from other aldehydes in the following respects:

(1) When treated with *alkalis*, it **does not resinify**, but is converted into methyl alcohol and alkali formate :

$$2HCHO + KOH \longrightarrow CH_3OH + HCOOK$$

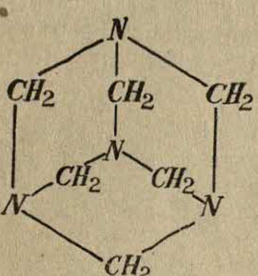
This reaction is known as **Cannizzaro's reaction** after its discoverer, and is also given by aromatic aldehydes.

In contact with baryta water, formaldehyde undergoes aldol condensation, yielding a mixture of sugars called *formose* or *a-acrose.*

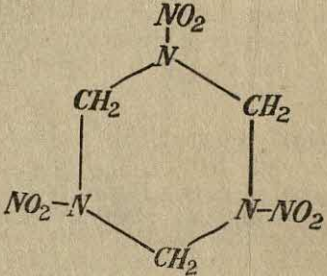
(2) With *ammonia*, formaldehyde does not yield an aldehyde ammonia, but gives a complex, crystalline substance, **hexamethylenetetramine** :—

$$6HCHO + 4NH_3 \longrightarrow C_6H_{12}N_4 + 6H_2O,$$

which, chiefly on the basis of X-ray examination, is assigned the structure shown below. It may be noted that the molecule of hexamethylenetetramine has a polycyclic structure composed of CH_2 groups bridged by nitrogen atoms into a cross-linked six-membered ring. There are in all four such rings of identical composition.



Hexamethylenetetramine



Cyclonite

In contact with acids, hexamethylenetetramine liberates formaldehyde. For this reason, it is employed as a convenient solid source of formaldehyde, and is used in various laboratory syntheses and in the manufacture of plastics and of the explosive **Cyclonite, RDX or hexogen.** This is produced by the action of fuming nitric acid on hexamethylenetetramine. Out of the four similar, 6-membered rings of the latter molecule *three* (does not matter which) are destroyed by oxidation of three methylene groups and one nitrogen atom. At the same time, the three nitrogen atoms of the remaining ring get nitrated (see the formula given above). The regular name of the product is **cyclotrimethylenetrinitramine**, but for the sake of brevity it is called "Cyclonite". It is a much more powerful explosive than T.N.T., and was produced on a very large scale during the Second World War for use in underwater operations and for demolitions.

Hexamethylenetetramine also finds use in (under the name **Urotropine**) as an internal disinfectant, especially for the urinary passage. Tablets of the drug are coated with an *enteric* coating (*i.e.*, a coating that prevents a drug from being attacked by gastric juice so long as in the stomach) of phenyl salicylate. On reaching the intestinal canal the coating gets dissolved and the drug is absorbed by the blood and taken to the urine. The acid present in the urine (which has been made acidic by a previous dose of sodium dihydrogen phosphate) brings about a slow liberation of formaldehyde, which acts as the antiseptic.

The reaction between formaldehyde and ammonium salts is *quantitative*,

$$4NH_4Cl + 6HCHO \longrightarrow (CH_2)_6N_4 + 6H_2O + 4HCl,$$

and the liberated acid can be titrated with standard alkali. Hence, this reaction is used for the estimation of an ammonium salt and also of formaldehyde solution.

(3) An aqueous solution of formaldehyde possesses the property of transforming proteins into a hard, elastic, rubber-like mass, quite insoluble in water.

Tests. Formaldehyde may be identified by the following tests :

(1) Silver-mirror Test (p. 275).

(2) Reduction of Fehling solution (p. 276).

(3) Schiff's Test (p. 281).

(4) **Rimini's Test.** If to an aqueous solution of formaldehyde two drops of phenylhydrazine be added, and then a drop of dilute, freshly prepared solution of **sodium nitroprusside** and a few drops of sodium hydroxide, a deep blue colour is produced, which changes through green and brown to red.

(5) **Milk Test.** If to a solution, containing formaldehyde, milk and ferric chloride, concentrated sulphuric acid be added carefully, a violet colour develops at the junction of the two layers. The test applies only to formaldehyde. It is a most ready test for detecting the presence of formaldehyde in milk (which has been illegally preserved with formaldehyde).

Uses. Formaldehyde is employed in commerce usually as a 40 per cent aqueous solution, called **Formalin.** The following are its more important uses:

(1) As a *disinfectant.* Formalin diluted with water is used for sterilizing surgical instruments, whilst paraformaldehyde or "**Paraform**" because of its ready conversion into gaseous formaldehyde, is employed for disinfecting rooms.

(2) On account of its power of *rendering proteins insoluble in water*, it is employed for the preservation of anatomical specimens and for *fixing* the gelatin film on photographic plates.

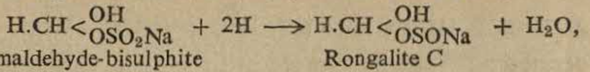
(3) Formaldehyde is also employed in the manufacture of—

(*i*) **Urotropine** and **cyclonite** (p. 284),

(*ii*) **Bakelite**, a hard, resinous material obtained by the condensation of formaldehyde with phenol and used as an insulating material ;

(*iii*) **Galalith**, a tough, horny material got by the action of formaldehyde on casein of milk and employed as artificial horn or ivory.

(*iv*) **Rongalite C**, a compound obtained by boiling a solution of the bisulphite compound of formaldehyde with zinc dust,



$$\underset{\text{Formaldehyde-bisulphite}}{H.CH{<}{}^{OH}_{OSO_2Na}} + 2H \longrightarrow \underset{\text{Rongalite C}}{H.CH{<}{}^{OH}_{OSONa}} + H_2O,$$

and used as a reducing agent in the decolorization of vat-dyes.

16. Acetaldehyde, Ethanal, $CH_3.CHO$.—

Laboratory Preparation. Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with potassium dichromate and dilute sulphuric acid. To avoid further oxidation of the aldehyde, an excess of alcohol is employed.

Expt. 8. A 1½ litre distillation flask is fitted with a dropping funnel, and is connected to a condenser and a receiver, the latter being cooled by a freezing mixture (Fig. 2).

100 grams of coarsely powdered potassium dichromate and 400 ml. of water are placed in the flask, which is gently heated on a stand-bath, until the liquid just boils. A mixture of 120 ml. of alcohol and 80 ml. of concentrated sulphuric acid is then slowly run in from the tap funnel. During the addition, the reaction should proceed at such a rate as to keep the liquid boiling. When all the mixture has been added, the boiling is continued, until about 150 ml. of the distillate have been collected. The distillate contains water and alcohol in addition to acetaldehyde.

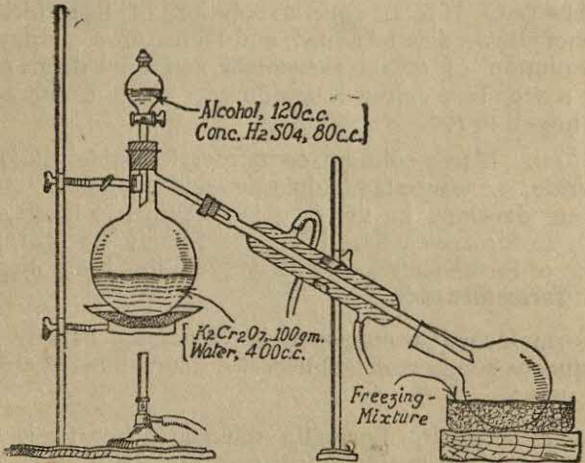


Fig. 2. Preparation of Acetaldehyde.

The aldehyde cannot be completely separated from this mixture by fractional distillation. It is, therefore, purified by conversion into aldehyde-ammonia. The process consists of the following three steps :—

(*i*) *Preparation of Ethereal Solution.* The flask containing the crude aldehyde is fitted with a reflux condenser (Fig. 3). The upper end of the condenser is connected by means of a long tube to two "reversed" wash-bottles, each containing about 50 ml. of ether, and cooled by a freezing mixture. The condenser is supplied with water at 30—36°C. A few glass beads are placed in the flask, and the liquid gently boiled for 15 minutes. During this time, most of the acetaldehyde (b.p. 21°C) would have passed over into ether. Alcohol and water condense and fall back into the flask.

(*ii*) *Saturation with Ammonia.* The ethereal solution of acetaldehyde, prepared as above, is now saturated with *dry* ammonia, the passage of which is continued, until the solution smells strongly of ammonia. The solution is left in the freezing mixture for an hour or so, when crystals of acetaldehyde-ammonia separate out. These are filtered at the pump, washed with a little dry ether, and finally dried in a desiccator.

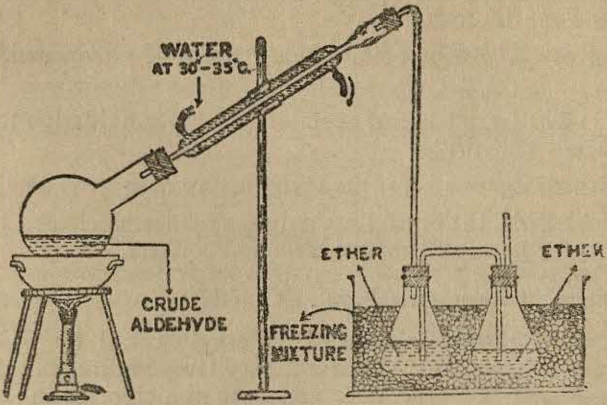


Fig. 3. Preparation of Acetaldehyde-ammonia.

(*iii*) *Decomposition of Aldehyde-Ammonia.* The aldehyde-ammonia is now distilled with dilute sulphuric acid from a water bath ; and the evolved aldehyde is collected in a well-cooled receiver. The distillate is dried over anhydrous calcium chloride and redistilled.

Commercial Preparation. Two processes are in use for the preparation of acetaldehyde on the commercial scale :—

(1) *By oxidation of Ethyl Alcohol.* The oxidation is effected either with dichromate and sulphuric acid, or preferably with air in the presence of heated metals as catalysts.

(2) *By Catalytic Hydration of Acetylene.* The reaction,

$$HC{\equiv}CH + H_2O \longrightarrow CH_3.CHO,$$

is brought about by means of 20 per cent sulphuric acid containing a small quantity of mercuric sulphate in solution. The gas is passed up a packed tower, down which the catalyst solution is flowing. Some of the mercuric salt gets reduced to metallic mercury. This is periodically removed from the bottom of the tower and converted to mercuric sulphate by treatment with nitric and sulphuric acids.

By-product Acetaldehyde. Some acetaldehyde is also obtained as a by-product in the manufacture of ethyl alcohol.

Properties. Acetaldehyde is a colourless, mobile liquid possessing a characteristic, suffocating odour and boiling at 21°C. It is readily soluble in water, alcohol and ether.

Tests. Besides the usual tests of an aldehyde, acetaldehyde gives the following specified tests :

(1) It gives a cherry-red colour with a solution of sodium nitroprusside and caustic soda.

(2) It gives a blue colour with sodium nitroprusside and piperidine.

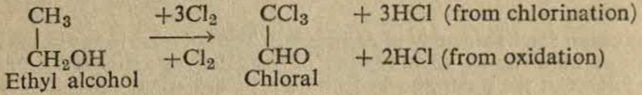
Uses. (1) The largest use of acetaldehyde is for oxidation to acetic acid and acetic anhydride.

(2) Another large use is for the manufacture of *n*-butyl alcohol.

(3) Metaldehyde, the crystalline polymer of acetaldehyde, is used as solid fuel for portable spirit burners and cookers.

17. Chloral, Trichloroacetaldehyde, $CCl_3.CHO$.—

Preparation. Chloral is obtained from ethyl alcohol by prolonged action of dry chlorine, first at the ordinary temperature, and then at the boiling point. Chlorine here acts both as a chlorinating and an oxidizing agent :



$$\begin{array}{cccl} CH_3 & +3Cl_2 & CCl_3 & +\ 3HCl\ \text{(from chlorination)} \\ | & \longrightarrow & | & \\ CH_2OH & +Cl_2 & CHO & +\ 2HCl\ \text{(from oxidation)} \\ \text{Ethyl alcohol} & & \text{Chloral} & \end{array}$$

The crystalline reaction product, which consists mainly of **chloral alcoholate.** $CCl_3CH{<}\genfrac{}{}{0pt}{}{OH}{OC_2H_5}$, is distilled with concentrated sulphuric acid. The oily distillate of crude chloral is converted into chloral hydrate, $CCl_3CH(OH)_2$. This is purified by recrystallization and then distilled with sulphuric acid, when pure chloral passes over.

Physical Properties. Chloral is an oily liquid of penetrating odour (b.p. 97°).

Reactions. Chloral possesses the general reactions of an aldehyde ; it gives the silver mirror test, combines directly with ammonia, hydrogen cyanide, sodium bisulphite, etc., and reacts with hydroxylamine and phenylhydrazine. On oxidation with concentrated nitric acid, it yields tetrachloroacetic acid :—

$$CCl_3CHO + O \longrightarrow CCl_3COOH$$

When boiled with a solution of potassium hydroxide, chloral decomposes to give chloroform and potassium formate :—

$$CCl_3CHO + KOH \longrightarrow CHCl_3 + HCOOK$$

The reaction is often employed for preparing pure chloroform.

18. Chloral Hydrate, $CCl_3CHO.H_2O$, or $CCl_3CH(OH)_2$.—As already mentioned, chloral combines with one molecular proportion of water, yielding chloral hydrate. The substance forms colourless crystals, readily soluble in water and melting at 57°.

Constitution. As chloral hydrate is stable enough to be isolated and melts without decomposition, it is generally assigned the

orthoaldehyde structure, $CCl_3.CH(OH)_2$, in which *two* hydroxyl groups are linked with one and the same carbon atom (a phenomenon that is of rare occurrence among organic compounds). The formula is supported by the following facts :—

(1) Chloral hydrate does not give Schiff's aldehyde reaction.

(2) It gives a *stable* hemiacetal (chloral alcoholate).

The following facts, on the other hand, indicate that chloral hydrate possesses the **aldehyde structure**, $CCl_3CHO.H_2O$:—

(1) It reduces ammoniacal silver nitrate.

(2) It reacts with hydroxylamine to give an oxime.

(3) The molecule of water is split out at the boiling point and on treatment with strong dehydrating agents (*e.g.*, cold, concentrated sulphuric acid).

Use. Chloral hydrate is used in medicine as a soporific.

19.—Acetone. *Dimethyl Ketone*, *Propanone*, $CH_3.CO.CH_3$.—

Occurrence. Acetone occurs in minute quantities in blood and normal urine. In pathological cases, *Diabetes mellitus* and *Acetonuria*, the proportion is much greater.

Laboratory Preparation. See Expt. 9, page 290.

Manufacture. Though present in considerable quantities in the distillate from the wood-distillation process, it is difficult to isolate acetone from it in a state of purity. So, the process is of little use from the industrial point of view at present ; it is only of historical interest.

(1) **Petrochemical Method.** The most important source of acetone at the present time is propylene obtained from the petroleum cracking process. The alkene is first converted into isopropyl alcohol, as already described (p. 245), which is then submitted to catalytic dehydrogenation with pieces of brass as catalyst :—

$$(CH_3)_2CHOH \longrightarrow CH_3.CO.CH_3 + H_2$$

(2) **From Acetic Acid.** Another important source of commercial acetone is acetic acid. The vapour of the acid is passed at about 480° over alumina (or lime-magnesia mixture), when it decomposes according to the equation,

$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O.$$

(3) **By Fermentation of Starch.** Some acetone (about 5 per cent of the total) is also obtained as a co-product in the production of butanol by the fermentation of starch.

Physical Properties. Acetone is a colourless liquid with a pleasant, aromatic odour. It boils at 56°, and the vapour is readily inflammable. It is miscible with water, alcohol and ether in all proportions.

Reactions. Besides all the general reactions of ketones already described, acetone, being a *methyl* ketone, gives the **Holoform Reaction** (p. 204). Hence, it can be employed in the preparation of both chloroform and iodoform, and may be detected by the *iodoform reaction.*

Expt. 9. *Laboratory Preparation and Properties of Acetone.*—Heat 50 gm. of dry calcium acetate in a retort attached to a Liebig condenser (Fig. 4). Dilute the distillate, which contains some tarry matter, with an equal volume of water, and then filter through a fluted filter to remove the tarry matter.

Show the presence of acetone in the aqueous solution, obtained as above, by the following tests :—

(1) **Legal's Test.** Take about 5 ml. of the solution in a test-tube, add about 1 ml. of sodium hydroxide and then about 5 drops of a freshly prepared solution of sodium nitroprusside (5 per cent). A ruby-red colour is produced which fades to yellow on standing.

Repeat the above test, and acidify the solution at once with acetic acid. A purple red colour is produced.

(2) **Iodoform Reaction.** Acetone gives iodoform reaction in the cold. Take about 2 ml. of dilute acetone solution, add about 5 drops of sodium hydroxide and then add a decinormal iodine solution, drop by drop, until the liquid becomes faintly yellow. There occurs an immediate separation of a pale yellow, micro-crystalline precipitate of iodoform (note smell).

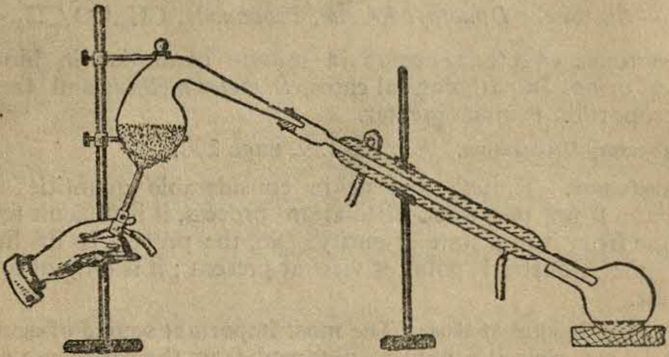


Fig. 4. Preparation of Acetone from Calcium Acetate.

Repeat the above test, using ammonia instead of sodium hydroxide. On adding iodine, drop by drop, a small amount of a black precipitate of nitrogen iodide is formed. Allow to stand, or warm. The precipitate disappears and iodoform is produced. This reaction serves to distinguish acetone from ethyl alcohol.

(3) **Formation of Indigo.** Dissolve a small quantity of *o*-nitrobenzaldehyde in about 1 ml. of acetone, stir the solution into about 100 ml. of water containing a little sodium hydroxide. Notice the rapid formation of indigo blue.

Uses. (1) Acetone is an important solvent, and is used in the preparation of high-class varnishes, cordite, and collodion, and for storing acetylene. It is also employed for extracting resins from wood and for making paint and varnish removers.

(2) It is used in the preparation of chloroform, iodoform, sulphonal, ionone and Lucite, the well-known methacrylate resin.

UNSATURATED ALDEHYDES AND KETONES

20. General.—Unsaturated aldehydes show the same chemical reactivity as saturated aldehydes. Further, on account of the presence of double and triple bonds, they also undergo the addition reactions characteristic of the unsaturated hydrocarbons from which they are derived.

21. Acrolein, *Acrylic Aldehyde*, *Propenal*, $CH_2{=}CH\ CHO$.—This is the simplest unsaturated aldehyde. It is obtained by removing the elements of water from glycerol, this being usually effected by distilling glycerol with potassium hydrogen sulphate :

$$\underset{\text{Glycerol}}{CH_2(OH).CH(OH).CH_2OH} \longrightarrow \underset{\text{Acrolein}}{CH_2{=}CH.CHO} + 2H_2O$$

Expt. 10. Heat a mixture of glycerol with about one-fifth its weight of crystallized potassium bisulphate. The vapour evolved has an unpleasant odour and attacks the eyes. Notice the action of the vapour on a drop of bromine water held on a glass rod.

Manufacture. There are two processes, now in use, for the preparation of acrolein on the commercial scale:

(1) **Direct Oxidation of Propylene.** In this method propylene, from petroleum refining, mixed with air, is passed over a catalyst, consisting of cuprous oxide supported on a porous form of fused alumina, at a temperature range of 300-350°C. Besides the main reaction,

$$CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO + H_2O,$$

other reactions occur at the same time, resulting in the production of small quantities of propionaldehyde, acetone, acetaldehyde and formaldehyde. The gas issuing from the converter is first cooled and then scrubbed with water to dissolve out the products. The resulting aqueous solution is submitted to fractionation to recover acrolein and other products.

(2) **Aldol Condensation of Acetaldehyde and Formaldehyde.** In this process an equimolecular mixture of acetaldehyde and formaldehyde in the vaporous state, is passed over a dehydration catalyst (lithium phosphate on activated alumina or sodium silicate on silica-gal) kept at a temperature range of 300—350°C:—

$$CH_2{=}\underset{\uparrow}{O} + \underset{|}{H}CH_2CHO \longrightarrow \underset{\text{unstable}}{CH_2(OH)CH_2CHO} \dashrightarrow \underset{\text{acrolein}}{CH_2{=}CHCHO}$$

Properties. (1) Acrolein is a colourless oily liquid, having an extremely pungent odour, hence the name (*acer*, pungen ; *oleum*, oil). The irritating, unpleasant odour produced when a vegetable-oil lamp or a tallow candle is put out is due to the formation of this substance. When brought in contact with the skin, it produces sores, and its vapour causes a plentiful flow of tears. It boils at 50°.

(2) Like other aldehydes, acrolein gives the silver mirror test and Schiff's magenta test. Its tendency to polymerize is so great that it

usually changes in a short time to an amorphous, brittle substance called **disacryl.** It is readily oxidized, even on exposure to air, to form acrylic acid.

(3) In addition to the aldehydic characters, acrolein shows the behaviour of an unsaturated compound. Thus, with bromine it gives the dibromide $CH_2Br.CHBr.CHO$. Catalytic hydrogenation in the presence of nickel at 50° to 60° converts it into propionaldehyde, $CH_3CH_2.CHO$. With hydrobromic acid it yields β-bromo-propionaldehyde, $CH_2Br.CH_2.CHO$ (compare action of HBr on acrylic acid). Acrolein combines with *two* molecules of sodium bisulphite instead of one. When the resulting addition compound is treated with acids, acrolein is *not* regenerated, only one molecule of the bisulphite being eliminated. This shows that the second molecule of sodium bisulphite must have been added at the double bond.

Uses of Acrolein :—

(1) The most important application of acrolein at the present time is in the manufacture of a sulphur-containing synthetic amino-acid called **Methionine** (α-Amino-γ-methylthiolbutyric acid), which is added to chicken feed (one pound, or less, per ton) to accelerate growth.

(2) Another use is in the manufacture of resins.

22. Crotonaldehyde, 2-*Butenal*, $CH_3.CH{=}CH.CHO$. Crotonaldehyde, also called *Crotonic Aldehyde*, is prepared on a large-scale from acetaldehyde by aldol condensation followed by dehydration in a single continuous operation (see page 278) :—

$$2CH_3.CHO \longrightarrow \underset{\text{Acetaldol}}{CH_3.CH(OH).CH_2.CHO} \xrightarrow{-H_2O} \underset{\text{Crotonaldehyde}}{CH_3.CH{=}CH.CHO}$$

It is employed in the manufacture of butanol-1.

Crotonaldehyde is a pungent-smelling liquid (b.p. 150°) closely resembling acrolein in its chemical behaviour. On oxidation with silver oxide, it yields **solid crotonic acid,** $CH_3.CH{=}CH.COOH$.

DIALDEHYDES AND DIKETONES

23. General.—Dialdehydes and diketones are of considerable interest, as they are valuable starting points for the syntheses of a variety of cyclic compounds. The dialdehydes may be obtained by Rosenmund's method, *i e.*, by the reduction of corresponding acid chlorides by means of hydrogen in the presence of finely divided palladium.

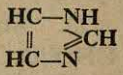
According to the relative position of the two CO groups diketones are classified as α- or 1 : 2-diketones, β- or 1 : 3 diketones, and γ- or 1 : 4-diketones. According to the Geneva nomenclature, diketones are named after the corresponding hydrocarbons by using the termination **-dione**. The α-diketones are yellow, volatile liquids having a pungent smell, while β- and γ-compounds are colourless, pleasant-smelling liquids.

24. Glyoxal, *Oxalic Aldehyde, Ethandial,* CHO.CHO.—When ethylene glycol, ethyl alcohol or acetaldehyde is carefully oxidized with nitric acid, a polymer of glyoxal, $[(CHO)_2]_n$, called **poly-glyoxal**[1], is obtained. When this is heated with phosphorus pentoxide, the monomeric glyoxal results.

Glyoxal is a yellow liquid (freezing-point 15° ; b.p. 51°). The vapour of glyoxal has an intense emerald green colour ; on condensation, the vapour yields at first a green liquid. This substance is unstable, and, even when kept in a strong freezing mixture, rapidly polymerizes to **para-glyoxal**, an insoluble modification of unknown molecular weight.

Glyoxal possesses the properties of an aldehyde. It reduces ammoniacal silver nitrate solution, and combines with two molecules of sodium bisulphite to form the crystalline **glyoxal sodium bisulphite,** $C_2H_2O_2.2NaHSO_3.H_2O$. It is by means of this derivative that glyoxal is usally isolated. Glyoxaloxime melts at 178° and the phenylhydrazone at 175°.

When treated with concentrated ammonia, glyoxal forms a cyclic base, called **glyoxaline**, which has the formula shown in the margin. It melts at 90° and boils at 263°.



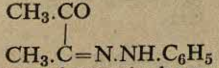
25. Diacetyl, *Biacetyl, Butanedione,* $CH_3.CO.CO.CH_3$.—Diacetyl is the simplest α-diketone. It is prepared from methyl ethyl ketone, *via* its monoxime. The ketone is treated with nitrous acid and the product is boiled with dilute sulphuric acid :

$$\underset{\text{Methyl ethyl ketone}}{CH_3.CO.CH_2.CH_3} \xrightarrow{HNO_2} \underset{\text{Diacetyl monoxime}}{CH_3.CO.C(:NOH).CH_3} \xrightarrow{\text{dil. }H_2SO_4} \underset{\text{Diacetyl}}{CH_3.CO.CO.CH_3}$$

Diacetyl is a yellow liquid with a pungent odour. It boils at 88° to give a vapour having the colour of chlorine. Its more important reactions are :

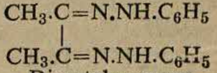
(1) With hydroxylamine, it forms the monoxime, $CH_3.CO.C(=NOH).CH_3$, and the dioxime, $CH_3.C(=NOH).C(=NOH).CH_3$.

(2) With phenylhydrazine, the monohydrazone and the dihydrazone (*osazone*) are produced :



$$\begin{array}{l} CH_3.CO \\ \quad | \\ CH_3.C{=}N.NH.C_6H_5 \end{array}$$

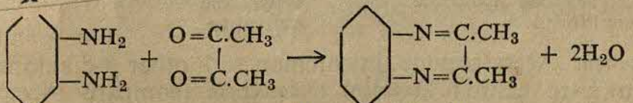
Diacetyl monohydrazone



$$\begin{array}{l} CH_3.C{=}N.NH.C_6H_5 \\ \quad | \\ CH_3.C{=}N.NH.C_6H_5 \end{array}$$

Diacetyl-osazone

(3) When treated with *o*-phenylenediamine, it forms the cyclic compound, **dimethylquinoxaline**,



o-Phenylenediamine Dimethyl quinoxaline

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[1] An amorphous substance, readily soluble in alcohol and ether.

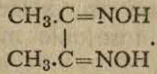
(4) In the presence of fermenting yeast it undergoes biochemical reduction :

$$\underset{\text{Diacetyl}}{CH_3.CO.CO.CH_3} + 2H \longrightarrow \underset{\text{2,3-Butanediol}}{CH_3.CH(OH).CH(OH).CH_3}$$

(5) Hydrogen peroxide decomposes diacetyl into two molecules of acetic acid :

$$CH_3.CO.CO.CH_3 + HO{-}OH \longrightarrow 2CH_3COOH$$

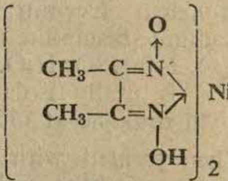
26. Dimethylglyoxime,



$$\begin{array}{l} CH_3.C{=}NOH \\ \quad | \\ CH_3.C{=}NOH \end{array}$$

. This substance being the dioxime of diacetyl, is obtained by the action of an excess of hydroxylamine on diacetyl. It is a colourless, crystalline powder, melting, with decomposition, at 285°.

Dimethylglyoxime is an important reagent for the detection and gravimetric estimation of nickel. It yields with the nickelous ion a red precipitate of the nickel complex shown in the margin. It is also used for the detection of bismuth salts with which it gives a yellow precipitate of the bismuth complex.



27. Acetylacetone, **2,4-Pentanedione,** $CH_3.CO.CH_2.CO.CH_3$.—This is one of the β-diketones prepared by condensing ethyl acetate with acetone in the presence of sodium :

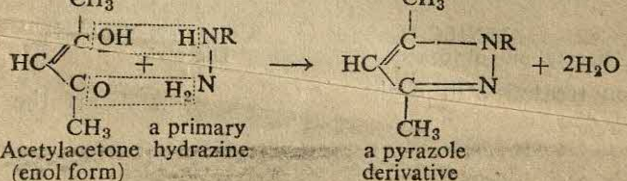
$$\underset{\text{Ethyl acetate}}{CH_3.COOC_2H_5} + CH_3.CO.CH_3 \xrightarrow{Na} \underset{\substack{\text{Sodio-derivative of}\\ \text{acetylacetone}}}{CH_3.C(ONa){=}CH.CO.CH_3}$$

The resulting sodium compound is then converted into the insoluble cupric salt, from which acetylacetone is liberated by treatment with dilute sulphuric acid.

Acetylacetone is a colourless, pleasant-smelling liquid, boiling at 137°. It is hydrolysed by boiling water into acetic acid and acetone.

$$CH_3.CO.CH_2.CO.CH_3 + HOH \longrightarrow CH_3COOH + CH_3.CO.CH_3$$

Acetylacetone, in common with other β-diketones, undergoes a large variety of condensations. Special mention may be made of its reaction with hydrazines. When **pyrazole derivatives** are produced :



Acetylacetone (enol form) a primary hydrazine a pyrazole derivative

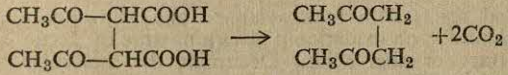
Constitution. Acetylacetone, in common with other β-diketones, has been shown to exhibit **keto-enol tautomerism** (compare Acetoacetic Ester)

$$\underset{\text{Diketo form}}{CH_3.CO.CH_2.CO.CH_3} \rightleftharpoons \underset{\text{Enol form}}{CH_3.C(OH){=}CH.CO.CH_3}$$

The power of the compound to form sodio-derivative and other metallic salts proves the existence of the enol form. Many of these metallic derivatives are insoluble in water but soluble in organic solvents, such as benzene and chloroform.

The **enol form** of acetylacetone can be obtained in the pure state by crystallizing the equilibrium mixture from petroleum ether at low temperatures.

28. **Acetonylacetone,** $CH_3.CO.CH_2.CH_2.CO.CH_3$, *2,5-Haxanedione*, is an example of a γ-diketone. It is usually prepared by heating diacetylsuccinic acid :



$$\begin{array}{l} CH_3CO—CHCOOH \\ \quad\quad\quad\quad | \\ CH_3CO—CHCOOH \end{array} \longrightarrow \begin{array}{l} CH_3COCH_2 \\ \quad\quad\quad\quad | \\ CH_3COCH_2 \end{array} + 2CO_2$$

Acetonylacetone is a colourless liquid with a pleasant smell, and is soluble in water, alcohol and ether. It boils at 190° under 750 mm.

Acetonylacetone, like other γ-diketones, is readily converted into derivatives of furane, thiophene and pyrrole.

QUESTIONS

1. (*a*) What are the general methods of obtaining aldehydes and ketones ?

(*b*) In what respects do aldehydes and ketones resemble and differ from one another ? (*Agra, B.Sc., 1960*)

2. Describe in detail the laboratory method for the preparation of an ethereal solution of pure acetaldehyde.

How does it react with (*a*) PCl_5, (*b*) $NaHSO_3$ and (*c*) dilute NaOH ? Give structural equations. (*Bihar, B.Sc., 1961*)

3. How is Acrolein prepared ? Describe its important properties and uses. (*Punjab, B.Sc., 1959*)

4. How is acetaldehyde prepared (*a*) in the laboratory (*b*) on commercial scale ?

In what respects does acetaldehyde differ in properties from formaldehyde ? Why is acetaldehyde given the structure CH_3CHO ? (*Rangoon, 1958*)

5. How is acetaldehyde prepared ? Compare its properties with those of acetone. (*Pondicherry, Pre-Professional, 1959*)

6. Describe the methods for the preparation of formaldehyde. Compare and contrast its properties with those of acetaldehyde. (*Punjab, B.Sc., Dairying, 1960*)

7. Describe in detail the laboratory method for the preparation of an ethereal solution of pure acetaldehyde.

Write structural equations to illustrate its reaction with (*a*) PCl_5. (*b*) HCN and (*e*) aqueous K_2CO_3. (*Bihar, B.Sc., 1956 Suppl.*)

8. Outline the methods by which aldehydes are generally prepared. In what respects does an aldehyde differ from a ketone ? (*Andhra, B.Sc., 1957*)

9. Give an account of the methods by which you can prove the structure of acetone. (*Patna, B.Sc., 1958*)

10. Give one method for the manufacture of (*a*) acetaldehyde, (*b*) acetone. Tabulate the reactions of these compounds in order to bring out points of similarity and dissimilarity. In what respects formaldehyde differs from acetaldehyde ? (*Mysore, B.Sc., 1958*)

11. An organic compound gave the following results on analysis :—

(*a*) 0·1475 gm. gave 0·088 gm. of carbon dioxide and 0·009 gram of water.

(*b*) 0·295 gm. gave 0·861 gm. of silver chloride.

(*c*) 0·1475 gm. displaced 24·6 ml. of air at 76 cm. at 27°C.

The compound on treatment with NaOH solution gave chloroform as one of the products of decomposition. Assign a structural formula to the compound.

Ans. Chloral, $CCl_3.CHO$. (*Bombay, 1932*)

12. A compound of carbon, hydrogen and oxygen gave following results on analysis : —

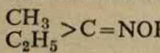
0·146 gm. gave 0·374 gm. CO_2 and 0·154 gm. H_2O, and the vapour density determination gave the value 42.

The compound reacts with hydroxylamine and with phenylhydrazine, but not with acetyl chloride ; on oxidation it gives a mixture of acetic acid and propionic acid with traces of other acids. Determine the molecular and structural formulae of the compound.

Ans. Methyl *n*-propyl ketone, $CH_3.CO.CH_2.CH_2\ CH_3$. (*Punjab, B.Sc., 1933*)

13. A ketoxime, on analysis, was found to possess the following composition : Carbon, 55·2 ; hydrogen 10·3 ; nitrogen, 16·1 per cent.

What is the formula of the compound and from what ketone is it derived ?

Ans. 
$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}C{=}NOH$; from methyl ethyl ketone.

14. A substance containing C, H and O only, gives on analysis, C=68·12% and H=13 64%. When gently oxidized, it is converted into a substance which gives C=69 77% and H=11 63%. The latter, on further oxidation under suitable conditions, gives a mixture which on analysis is found to consist of saturated fatty acids containing one, two, three and four atoms of carbon per molecule, but none of the higher acids. Suggest a constitutional formula for the substance and describe the tests you would employ to confirm it. (*Pembroke College, Cambridge*)

Ans. The secondary alcohol, $CH_3.CHOH.C_3H_7$, yielding the ketone $CH_3.CO.C_3H_7$.

15. The calcium salt of a monobasic acid containing C, H and O, when heated gave a distillate which reacted with hydroxylamine to give a derivative containing 10·85 per cent of nitrogen. Calculate the approximate molecular weight of (*a*) the nitrogen derivative and (*b*) the original acid, and suggest possible structural formula of each. (*Calcutta, B.Sc., 1943*)

16. An organic compound, *A*, which reduced Fehling's solution, on analysis was found to contain C=16·27%, H=3·68%, and Cl=72·20%. On oxidation it was converted to a monocarboxylic acid *B* having C=14·68%, H=0·61%, and Cl=65 14%. When distilled with soda-lime, it gave a sweet-smelling liquid *C* containing 89·12% chlorine. *A*, when heated with alkali, also gave the compound *C*. Explain the above reactions, and assign structural formulae to *A*, *B* and *C*. (*Allahabad, B.Sc., 1952*)

Ans. (*A*) CCl_3CHO ; (*B*) CCl_3COOH ; (*C*) $CHCl_3$.

17. Write explanatory notes on *any three* of the following topics : (*a*) Oppenauer oxidation, (*b*) Aldol condensation, (*c*) Clemmensen reduction, (*d*) Dehydration of alcohols, (*e*) Claisen reaction. (*Lucknow, B.Sc., Prev., 1962*)

18. An organic compound A has the molecular formula $C_3H_6Cl_2$. On reducing with Na and alcohol it gives propane (B). When A is boiled with alkali, a compound (C) having the formula C_3H_6O is formed. The latter reacts with NH_2OH and reduces Fehling's solution. Assign structures to A, B and C. (*Agra, B.Sc., 1958*)

Ans. (*A*) $CH_3CH_2CHCl_2$, (*B*) $CH_3CH_2CH_3$, (*C*) CH_3CH_2CHO.

19. An unsaturated ketone gave the following results on analysis : 0·1633 gm. gave 0·44 gm. CO_2 and 0·15 gm. H_2O. 1·96 gms. of the ketone on treatment with an excess of hydrocyanic acid gave 2 5 gm. of cyanhydrin. When oxidised with

$KMnO_4$ solution, the ketone gave acetone and a ketonic acid, which readily yielded on oxidation carbon dioxide and acetic acid. On treatment with hydroxylamine in alkaline solution, the ketone gave a compound having $C_6H_{16}O_2N$ as the molecular formula. Assign a structural formula to the ketone and to the product obtained by the action upon it of hydroxylamine. (*Bombay, B.Sc., 1941*)

20. 0·1588 gm. of an organic substance gave 0·3615 gm. of CO_2 and 0·1479 gm. of H_2O. Its V. D. was 29. The compound reduces Fehling's solution and on oxidation gave an acid, the silver salt of which contained 59·6% Ag. Give the name and structural formula of the compound.

Ans. Propionaldehyde. CH_3CH_2CHO. (*Agra, B.Sc., 1958*)

21. Two organic substances containing C, 62·1 ; H, 10·34 ; O, 27·6% with KCN and dilute H_2SO_4 yielded substances which on hydrolysis gave two isomeric monobasic acids with mol. wt. 104. Identify the two substances. How would the third isomer behave under similar conditions ? (*Nagpur, B.Sc., 1956*)

Ans. Molecular formula, C_3H_6O. The two substances are C_2H_5CHO and CH_3COCH_3. The third isomer, *viz.* allyl alcohol, $CH_2=CH.CH_2OH$, does not react with HCN.

22. Two isomeric neutral substances, *A* and *B*, contained 62·01% carbon and 10·35% hydrogen. Their vapour density is 29. On mild oxidation, *A* gives rise to a monobasic acid, *C*, containing 48·64% carbon and 8·11% hydrogen. The equivalent weight of *C* is found to be 74. On similar treatment, *B* remains unaffected, but it readily reacts with iodine and sodium hydroxide, producing iodoform. What are the structural formulae of *A* and *B* ?

Ans. (*A*) CH_3CH_2CHO (*B*) CH_3COCH_3. (*Delhi, B.Sc., 1959*)

23. A neutral organic compound, *A*, on analysis gave C, 52·17% ; H, 13·04%. On mild oxidation *A* gave another neutral compound *B*. With very dil. alkali, *B* gave rise to another compound *C* with double the molecular weight. *C* readily loses water on heating to form *D* which on oxidation gave crotonic acid. What are *A*, *B*, *C* and *D* ? (*Andhra, B.Sc , 1958*)

Ans. (*A*) Ethyl alcohol, C_2H_5OH. (*B*) Acetaldehyde, CH_3CHO. (*C*) Aldol, $CH_3CH(OH)CH_2CHO$. (*D*) Crotonaldehyde, $CH_3.CH=CH.CHO$.

24. Describe with formulae, what happens when the following reactions are carried out on acetaldehyde :—

(*i*) An oxidation reaction ;
(*ii*) A substitution reaction ;
(*iii*) A polymerisation reaction ;
(*iv*) A condensation reaction ;
(*v*) An addition reaction ? (*Jadavpur, B.Sc., 1962*)

25. Describe the laboratory preparation of a pure sample of acetone. Explain, with equations, its reactions with hydrocyanic acid, semicarbazide and phenylhydrazine. How do you identify a sample of acetone ? (*Gauhati, B.Sc., 1962*)

26. How is acetone prepared from acetic acid ? Indicate by equations how you can synthesise the following from acetone :—

(*a*) 1,1,2,2-Tetramethylethylene glycol ;
(*b*) α-Hydroxyisobutyric acid ;
(*c*) Mesityl oxide ;
(*d*) *t*-Butyl alcohol ;
(*e*) Isopropylamine. (*Jadavpur, B.Sc., 1962*)

27. A hydrocarbon, *A*, whose vapour density is 22, gives the following reactions :—

(*a*) On chlorination, a monochloro derivative, *B*, is formed.

(*b*) *B*, on hydrolysis and subsequent oxidation, gives acetone. Assign structural formulae to *A*, *B* and the product of hydrolysis. (*Agra, B.Sc., 1958*)

Ans. $CH_3CH_2CH_3$; $CH_3CH(Cl)CH_3$; $CH_3CH(OH)CH_3$

28. An organic compound (A) on analysis was found to contain C=16·271% ; H=0·677% ; and chlorine=72·203%. The compound reacted with Fehling's solution and on oxidation gave a compound (B) a monocarboxylic acid having C=14·679% ; hydrogen=0 612% ; and chlorine=65·137%. On heating with soda-lime the compound (B) gave a sweet smelling liquid (C), containing 89·12% of chlorine. The substance (C) can also be obtained from (A) on heating (A) with dilute alkali.

What structural formulae would you assign to (A), (B) and (C) and try to identify the compounds and explain the reactions ?

(*Vikram, B.Sc., 1960* ; *Agra, 1950* ; *Allahabad, 1952* ; *Delhi, 1956*)

Ans. (*A*) Chloral, CCl_3CHO (*B*) Trichloroacetic acid, CCl_3COOH (*C*) Chloroform, $CHCl_3$.

29. An organic compound, whose V.D. is 43, contains C=69·8, H=11·6 and O=18·6%. The compound reacts with hydroxylamine and phenylhydrazine. On oxidation, it gives a mixture of acids of which acetic acid and propionic acid predominate. What is the structural formula of the compound ?

Ans. $CH_3COCH_2CH_2CH_3$ (*Punjab, B.Sc., 1955*)

30. A ketoxime, on analysis, was found to possess the following composition : C, 55 2% ; H, 10·3% ; N, 16·1%. What is the formula of the compound and from what ketone is it derived ?

Ans. $\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}C{=}NOH$; $\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CO$. (*Calcutta, B.Sc., 1950*)

CHAPTER EIGHTEEN

MONOCARBOXYLIC ACIDS

1. General.—The characteristic group present in the carboxylic acids is the **carboxyl group**$-\mathrm{C}{\lt}^{\mathrm{O}}_{\mathrm{OH}}$. The term "*carboxyl*" is a contraction of *carbonyl* and *hydroxyl*, and is suggestive of the fact that the group is composed of the $C=O$ and OH groups. The carboxylic acids may be regarded as derived from the hydrocarbons, and represent the final stage in the oxidation of the terminal methyl group of the hydrocarbon molecule. The intermediate stages in the oxidation are represented by primary alcohols and aldehydes.

The carboxylic acids are divided into *monocarboxylic*, *dicarboxylic* and *tricarboxylic* acids, according as one, two or three carboxyl groups are present in the molecule. Non-substituted monocarboxylic acids are called **fatty acids**, on account of their frequent occurrence as glyceryl esters in fats and oils.

2. Nomenclature of Carboxylic Acids.—Four systems of nomenclature of carboxylic acids are in use :—

(1) **Common Names.** A good many of the monocarboxylic acids were originally isolated from various materials, and were assigned names usually derived from the source of origin. The following list illustrates this method of naming the acids and gives the structure, name and the source in each case :—

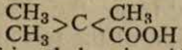
Structure	Common Name	Source
$H.COOH$	Formic acid	L. *formica*, ant.
$CH_3.COOH$	Acetic acid	L. *acetum*, vinegar.
$CH_3.CH_2.COOH$	Propionic acid	The word *propionic* is derived from the Greek for "first fat". This refers to the fact that the acid is the first of the series that can be "salted out" from an aqueous solution.
$CH_3.(CH_2)_2.COOH$	Butyric acid	L. *butyrum*, butter.
$CH_3.(CH_2)_3.COOH$	Valeric acid	*Valerian* root.
$CH_3.(CH_2)_4.COOH$	Caproic acid	The three acids, *caproic caprylic* and *capric* occur in butter-fat of goat's milk (L. *caper*, goat).
$CH_3.(CH_2)_6\ COOH$	Caprylic acid	
$CH_3.(CH_2)_8.COOH$	Capric acid	
$CH_3.(CH_2)_{10}.COOH$	Lauric acid	Oil of laurel.
$CH_3.(CH_2)_{12}.COOH$	Myristic acid	Fat of nutmegs from *Myristica fragrans*.
$CH_3.(CH_2)_{14}.COOH$	Palmitic acid	Palm oil.
$CH_3.(CH_2)_{16}.COOH$	Stearic acid	Gr. *stear*, fat.

In naming substituted acids, the position of the substituent on the carbon chain is defined by Greek letters, α, β, γ, δ, etc. The first carbon atom behind the carboxyl group is designated the α-carbon atom, the next β-, and so on. Thus, the acid with the structure $CH_3.CH_2.CHBr.CH(CH_3).COOH$ is called α-methyl-β-bromovaleric acid.

(2) **As Alkyl Derivative of Acetic Acid.** A convenient system of naming higher homologues is to regard them as alkyl derivatives of acetic acid. The following are a few examples :

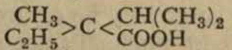
$CH_3.CH_2.COOH$
Methylacetic acid

$(CH_3)_2CH\ COOH$
Dimethylacetic acid



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\!\begin{matrix}CH_3\\COOH\end{matrix}$$

Trimethylacetic acid



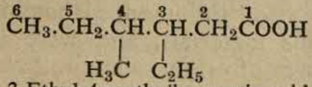
$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}CH(CH_3)_2\\COOH\end{matrix}$$

Methylethylisopropylacetic acid

(3) **Geneva Name.** In the Geneva System, the name of the acid is derived from the **longest chain of carbon atoms including the carbon of the COOH group** (compare aldehydes). The suffix for the series is **-oic acid.** The numbering of the carbon atoms is *always started from the carbon of the carboxyl group*, which is counted as carbon atom No. 1 (compare aldehydes). The following examples illustrate the system :

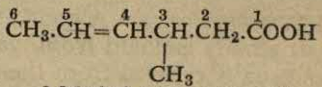
$H.COOH$
Methanoic acid

$CH_3.COOH$
Ethanoic acid



$$\overset{6}{C}H_3.\overset{5}{C}H_2.\underset{H_3C}{\overset{4}{C}}H.\underset{C_2H_5}{\overset{3}{C}}H.\overset{2}{C}H_2\overset{1}{C}OOH$$

3 Ethyl-4-methylhexanoic acid



$$\overset{6}{C}H_3.\overset{5}{C}H=\overset{4}{C}H.\underset{CH_3}{\overset{3}{C}}H.\overset{2}{C}H_2.\overset{1}{C}OOH$$

3-Methyl-4-hexenoic acid

(4) **As Carboxyl Derivative of Hydrocarbons.** Carboxylic acids may, of course, be named as carboxyl derivatives of hydrocarbons. Thus, we have :

$CH_3.COOH$	Methanecarboxylic acid
$C_2H_5.COOH$	Ethanecarboxylic acid

These names are frequently used and the student should clearly distinguish between them and the Geneva names. Thus, the Geneva name of *methane*carboxylic acid is *ethanoic* acid and of *ethane*carboxylic acid *propanoic* acid.

3. Acyl Groups.—The groups which would remain on removing the hydroxyl from fatty acid molecules are termed "acyl" groups. The name for each acyl group is derived from that of the corresponding acid by changing the termination *-ic* into *-yl* :

$HCO-$, Formyl
CH_3CO-, Acetyl
C_2H_5CO-, Propionyl,
C_3H_7CO-, Butyryl

1. SATURATED MONOCARBOXYLIC ACIDS

4. General Methods of Formation.—The methods for the synthesis of monocarboxylic acids may be divided into three classes :—

(1) **Methods in which the Number of Carbon Atoms remains Unaltered.** They are :—

(*i*) *By Oxidation of Primary Alcohols and Aldehydes ; e.g.*,

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + 2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

The oxidation can be conveniently carried out by means of potassium dichromate and dilute sulphuric acid.

(*ii*) *By Hydrolysis of Trihalogen Derivatives of Alkanes.* Trihalogen derivatives of alkanes, in which all the three halogen atoms are linked to the *same* carbon atom, when submitted to hydrolysis, give fatty acids ; *e.g.*,

$$\underset{\text{1,1,1-Trichloroethane}}{CH_3.CCl_3} \xrightarrow{HOH} \underset{\substack{\text{Orthoacetic acid}\\\text{(unstable)}}}{CH_3C(OH)_3} \xrightarrow{-H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$$

(*iii*) *By Hydrolysis of Esters.* When an ester of a fatty acid is submitted to hydrolysis, the acid is set free. The method is of special importance for the preparation of higher fatty acids present in fats and oils ; *e.g.*,

$$\underset{\text{Tristearin}}{(C_{17}H_{35}COO)_3C_3H_5} + 3HOH \longrightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

(2) **Carboxylations.** These involve the introduction of a new carbon atom in the form of carboxyl group :—

(*i*) *From Alkyl Halides through the Cyanide Synthesis.* When an alkyl halide is treated with potassium cyanide, we get an **alkyl cyanide** :—

$$\underset{\text{Methyl iodide}}{CH_3I} + KCN \longrightarrow \underset{\text{Methyl cyanide}}{CH_3CN} + KI$$

The cyanide, when submitted to hydrolysis with a dilute mineral acid or alkali, yields the corresponding fatty acid :—

$$CH_3CN + 2H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(*ii*) *From Alkyl Halides through Grignard's Reaction.* When an alkyl halide is treated with dry magnesium in the presence of dry ether, it gives an alkylmagnesium halide (Grignard's reagent) :

$$CH_3Br + Mg \longrightarrow CH_3MgBr$$

This absorbs carbon dioxide, yielding an addition compound. The latter when decomposed with dilute hydrochloric acid sets free the carboxylic acid :

$$CH_3MgBr + CO_2 \longrightarrow \underset{\text{Addition compound}}{CH_3COOMgBr}$$

$$CH_3COOMgBr + HCl \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + MgBrCl$$

(*iii*) *From Alkali Alcoholates by Absorption of Carbon Monoxide.* This occurs at high temperatures :—

$$\underset{\text{Sodium methoxide}}{CH_3ONa} + CO \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa}$$

(*iv*) *From Acid Chlorides by Condensation with Diazomethane.* A method of *converting a carboxylic acid into the next higher homologue* consists in treating its acid chloride with diazomethane (2 molecules), when a diazoketone is produced :—

$$\mathrm{RCOCl} + \underset{\text{Diazomethane}}{2\mathrm{CH_2N_2}} \longrightarrow \underset{\text{Diazoketone}}{\mathrm{RCOCHN_2}} + \mathrm{CH_3Cl} + \mathrm{N_2}$$

The diazoketone, when warmed with water in the presence of silver oxide as catalyst, loses nitrogen and adds on water to give the next higher carboxylic acid[1] :—

$$\mathrm{RCOCHN_2} + \mathrm{HOH} \longrightarrow \mathrm{RCH_2COOH} + \mathrm{N_2}$$

(3) **Partial Decarboxylation of Dicarboxylic Acids.** Dicarboxylic acids in which the two carboxyl groups are separated by not more than one carbon atom lose carbon dioxide on heating, yielding monocarboxylic acids :—

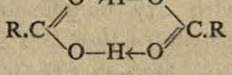
$$\underset{\text{Oxalic acid}}{\mathrm{HCOO.COOH}} \longrightarrow \underset{\text{Formic acid}}{\mathrm{HCOOH}} + \mathrm{CO_2}$$

$$\underset{\text{Malonic acid}}{\mathrm{HCOO.CH_2.COOH}} \longrightarrow \underset{\text{Acetic acid}}{\mathrm{CH_3COOH}} + \mathrm{CO_2}$$

$$\underset{\text{Methylmalonic acid}}{\mathrm{HCOO.CH(CH_3).COOH}} \longrightarrow \underset{\text{Propionic acid}}{\mathrm{CH_3CH_2COOH}} + \mathrm{CO_2}$$

5. Physical Properties.—The lower members of this series are colourless, corrosive liquids, possessing a strong, pungent odour. They distil without decomposition, and are readily soluble in water, the solutions showing an acid reaction. The members C_4 to C_9 are oily liquids, sparingly soluble in water and possessing an unpleasant, rancid odour. From C_{10} upwards they are waxy solids, practically insoluble in water, but readily soluble in alcohol and ether ; they can be distilled, without decomposition, only under reduced pressure, or in a current of steam.

Association. Molecular weights of lower members in non-ionizing solvents (*e.g.* benzene) possess about double the value calculated for single molecules. This is part of the evidence which leads us to believe that the acids exist mainly as *cyclic dimers* containing bicovalent hydrogen as shown below :



6. Chemical Properties of Carboxylic Acids.—The chemical properties of carboxylic acids are dependent on the carboxyl group that they contain. This group has been shown (see sec. 8) to possess the structure $-\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{OH}}$.

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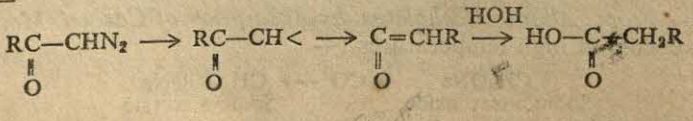
[1] The reaction, known as **Arndt-Eistert Reaction** (1935) involves a rearrangement :—



$$\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{RC}}\mathrm{—CHN_2} \longrightarrow \underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{RC}}\mathrm{—CH}< \longrightarrow \underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{=CHR} \xrightarrow{\mathrm{HOH}} \mathrm{HO—}\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{—CH_2R}$$

(1) **Reactivity of Carboxylic Hydrogen.** Carboxylic acids possess an acidic character. In aqueous solution, they undergo ionization, though to a very small extent :

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

The replacement of the carboxylic hydrogen by metals gives rise to salts that are strongly hydrolysed by water.

(2) **Reactions of Carboxylic Hydroxyl Group.** The *hydroxyl* component of the carboxyl group is very reactive, and may be replaced by many other atoms or groups. Thus, we have :

(*i*) *Reaction with Phosphorus Halides.* These react with carboxylic acids in the same way as with alcohols, giving *acid chlorides*, R.COCl, *acid bromides*, R.COBr, and *acid iodides*, R,COI. Thus, phosphorus pentachloride and acetic acid react in accordance with the following equation :

$$CH_3COOH + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

(*ii*) *Esterification.* The reaction between a carboxylic acid and an alcohol involves the replacement of the carboxylic hydroxyl group by an *alkoxyl* group, RO, resulting in the formation of an ester. Formerly, it was believed that esterification involved the *hydrogen* atom of the carboxyl group and the hydroxyl of the alcohol. This, however, has been shown to be incorrect (see page 231).

(*iii*) *Amide Formation,* When a carboxylic acid is treated with ammonia and the resulting ammonium salt heated, we get an *acid amide*, the net effect being the replacement of the hydroxyl by the NH_2 group :—

$$CH_3CO\boxed{OH + H}NH_2 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(3) **Reduction of Carboxyl Group.** The carboxyl group is very resistant to the action of common reducing agents. However, reduction is possible under certain conditions :—

(*i*) Prolonged heating with hydriodic acid and phosphorus causes *reduction of the carboxyl to the methyl group*. In the case of the lower members, the reduction does not proceed very smoothly ; higher members respond better.

(*ii*) Carboxylic acids can be reduced to *primary alcohols* by treatment with hydrogen, using high pressures, high temperatures and catalysts (Ni, Co, Cu)[1]. Higher primary alcohols (employed in the manufacture of detergents) are nowadays produced on commercial scale by this process.

(*iii*) A more recent method of directly reducing carboxylic acids to *alcohols* is by means of lithium-aluminium hydride, $LiAlH_4$ (p. 227).

---

[1] Guyer (1955) has shown that this reaction can be readily brought about in the presence of a ruthenium or copper-chromium catalyst.

(*iv*) Esters of carboxylic acids are more easily reduced than the acids themselves. Treatment with sodium and alcohol gives a 70 to 80 per cent yield of primary alcohol :—

$$R.COOC_2H_5 + 2H \longrightarrow R.CH_2OH + C_2H_5OH$$

(*v*) An indirect method of bringing about reduction of carboxylic acids, due to **Rosenmund**, consists in converting the acid into its chloride and submitting the latter to catalytic reduction with hydrogen, when an *aldehyde* is produced (p. 269).

(*vi*) Reduction of carboxylic acids to *aldehydes* can also be effected by means of formic acid. A mixture of vapours of the acid to be reduced and formic acid is passed over titanium oxide (catalyst) heated at 330°, when the carboxyl group of the acid concerned is reduced to the aldehyde group, while formic acid is oxidized to carbon dioxide :

$$\begin{array}{l} RCO\vdots OH \\ \quad +H\vdots COOH \end{array} \longrightarrow RCHO + CO_2 + H_2O$$

Alternatively, a mixture of the calcium salt of the acid is distilled with calcium formate :

$$(RCOO)_2Ca + (HCOO)_2Ca \longrightarrow 2RCHO + 2CaCO_3$$

(4) **Decarboxylation.** The decarboxylation of carboxylic acids and their conversion into other types of compounds may be effected by the following methods :—

(*i*) Kolbe's electrolytic method of converting a carboxylic acid into a *higher hydrocarbon* (method 4, p. 137).

(*ii*) Dumas' methods of converting a carboxylic acid into a *hydrocarbon containing one carbon less* than the acid itself. It consists in heating an alkali salt of the acid with soda lime [method 5(*i*), p. 138].

(*iii*) Conversion of carboxylic acids into *ketones* by pyrolysis of the acids (p. 269) or by dry distillation of their calcium salts (page 268).

(*iv*) An indirect method of replacing the carboxyl group by the *amino group* consists in converting an acid into its amide and treating the latter with bromine and aqueous potash (Hofmann's Bromamide Reaction (*see* chap. 19, sec. 12).

(5) **Reactions involving the Alkyl Group of Carboxylic Acids.** The effect that the carboxyl group exerts on the reactivity of the alkyl group is noteworthy. In certain reactions, the *alpha* CH_2 group is found to be the most reactive ; in others the *beta* position is found to be the most favoured. The following are the more important examples :—

(*i*) **Halogenation.** With the chlorine or bromine in presence of a catalyst (iodine or phosphorus), the hydrogen attached to the *alpha*-carbon atom is replaced much more readily than the other hydrogen atoms of the alkyl group ; *e.g.*,

$$\underset{\text{Propionic acid}}{CH_3.CH_2.COOH} \xrightarrow{Br_2} \underset{\alpha\text{-Bromopropionic acid}}{CH_3.CHBr.COOH} \xrightarrow{Br_2} \underset{\alpha\text{-Dibromopropionic acid}}{CH_3.CBr_2.COOH}$$

(*ii*) **Condensation with Esters.** An important reaction of the *alpha*-CH_2 group is the condensation with esters of carboxylic acids under the influence of sodium ; *e.g.*,

$$CH_3.CO\boxed{OC_2H_5+H}CH_2.COOC_2H_5 \xrightarrow{Na} CH_3.CO.CH_2.COOC_2H_5 + C_2H_5OH$$

For the mechanism of this reaction, see under Acetoacetic Ester.

(*iii*) **Oxidation at β-Position.** Biochemical experiments have shown that the *beta* position of a carboxylic acid is the most reactive towards oxidation. Thus, in the body of a diabetic person, butyric acid, $CH_3.CH_2.CH_2.COOH$, is converted into β-hydroxybutyric acid, $CH_3.CH(OH).CH_2.COOH$.

Treatment with certain oxidizing agents also results in *beta*-oxidation of carboxylic acids. Thus, 3 per cent hydrogen peroxide causes the oxidation of butyric acid first to β-hydroxybutyric acid and then to acetoacetic acid, $CH_3.CO.CH_2.COOH$.

7. Detection and Identification of Carboxylic Acids.—The presence of an **acidic substance** is indicated by the following facts :—

(1) If it is insoluble in water but soluble in dilute alkali solution ; or

(2) If it is soluble in water and the aqueous solution requires an appreciable amount of alkali for neutralization to phenolphthalein.

Since some other types of organic compounds, of which *sulphonic acids* and *phenols* are the commonest, also behave like carboxylic acids, it is necessary **to make a distinction.** This is done as follows :—

(*a*) The absence of sulphur in elementary qualitative analysis excludes the presence of a sulphonic acid.

(*b*) The failure of the compound to give either the bromine water test or the ferric chloride test excludes the presence of a phenol.

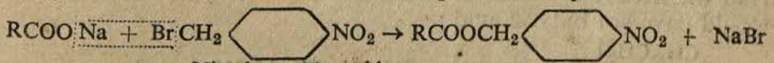
The next step is **to identify the carboxylic acid** present. This is done as follows :—

(*i*) The equivalent weight of the acid is determined accurately by means of standard barium hydroxide, using phenolphthalein as the indicator.

(*ii*) If the acid is a crystalline solid, its melting point is determined.

(*iii*) If it is a liquid, it is converted into a **solid derivative** having a sharp melting point. For this purpose, the following derivatives are the most suitable :—

(*a*) The ester of the acid with *p*-nitrobenzyl alcohol is prepared by heating the sodium salt of the acid with *p*-nitrobenzyl bromide :

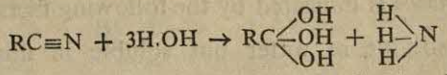


p-Nitrohenxyl bromide solid ester

(*b*) The amide (or the anilide) of the acid is prepared by treating the chloride of the acid (obtained from the acid by the action of phosphorus pentachloride) with ammonia (or aniline):—

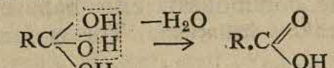
$$\mathrm{RCOCl} + \mathrm{NH_3} \rightarrow \underset{\text{amide}}{\mathrm{RCONH_2}} + \mathrm{HCl}$$

8. Constitution.—The constitution of fatty acids follows from their synthesis from alkyl cyanides (sec. 4). When an alkyl cyanide, $\mathrm{R.C{\equiv}N}$, is heated with an alkali, or a dilute mineral acid, we get a molecule each of ammonia and a fatty acid. Since the acid produced has the same number of carbon atoms in the molecule as the alkyl cyanide, the carbon chain must have remained intact, the cleavage occurring at the $\mathrm{C{\equiv}N}$ linkage. The hydrolysis may be explained by assuming the molecule of the water to be split into hydrogen and hydroxyl: the hydrogen atom, being electropositive, goes to the electronegative nitrogen atom, while the hydroxyl goes to the carbon. By a three-fold repetition of this process, we get a molecule each of ammonia and a trihydroxy compound containing the three hydroxyls linked to the same carbon atom :



$$\mathrm{RC{\equiv}N} + \mathrm{3H.OH} \rightarrow \mathrm{RC}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{smallmatrix} + \begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{smallmatrix}\!\!>\!\mathrm{N}$$

But since the acid produced is not $\mathrm{R.CO_3H_3}$ but $\mathrm{R.CO_2H}$ (*i.e.*, it contains one molecule of water less), we must assume that the trihydroxy compound, like most others containing more than one hydroxyls linked to the same carbon atom, loses a molecule of water as shown below :—



$$\mathrm{RC}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O\,H}\\ \mathrm{OH}\end{smallmatrix} \xrightarrow{-\mathrm{H_2O}} \mathrm{R.C}\begin{smallmatrix}\mathrm{O}\\ \\ \mathrm{OH}\end{smallmatrix}$$

Hence the acid obtained possesses the above structure, *i.e.*, it contains a **carboxyl group**, $-\mathrm{C}\begin{smallmatrix}\mathrm{O}\\ \mathrm{OH}\end{smallmatrix}$.

The above view of the constitution of the carboxyl group is fully supported by the reactions of these acids (sec. 6). Thus the presence of a hydroxyl in the carboxyl group is proved by the action of phosphorus pentachloride, which gives rise to an acid chloride, R.CO.Cl. Further, the replacement, by the metal, of only *one* of the hydrogen atoms present in the molecule shows that this one is in a different state of combination from the rest, *i.e.*, the replaceable hydrogen atom forms a part of the carboxyl group. The truth of this assumption has been formally proved by the interaction of silver acetate and ethyl iodide, when ethyl acetate is formed :

$$\begin{matrix}\mathrm{CH_3COO\,\vdots\,Ag}\\ +\mathrm{C_2H_5\,\vdots\,I}\end{matrix} \rightarrow \underset{\text{Ethyl acetate}}{\mathrm{CH_3COOC_5H_5}} + \mathrm{AgI}$$

Had the silver atom been attached to the methyl-carbon atom we would have got butyric acid :

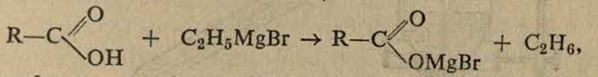
$$\mathrm{CH_3.CH_2\,\vdots\,I} \atop {+\,\vdots\,\mathrm{Ag}\,\vdots\,\mathrm{CH_2COOH}} \rightarrow \underset{\textbf{Butyric acid}}{\mathrm{CH_3CH_2.CH_2COOH}} + \mathrm{AgI}$$

Cause of Low Reactivity of the Carbonyl Component of the Carboxyl Group.— The following points indicating comparative inertness of the carbonyl part of the carboxylic acids may be noted :

1. The carboxyl group, >C=O, constitutes the *unsaturated* part of the carboxyl group, and we would therefore expect carboxylic acid to possess as much reactivity towards the typical carbonyl reagents (hydroxylamine, sodium bisulphite, phenylhydrazine, etc.) as aldehydes and ketones do But, carboxylic acids are altogether inert towards these reagents.

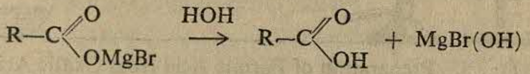
2. The carbonyl component of carboxylic acids is very much resistant to the common methods of reduction applicable to aldehydes, ketones and esters.

3. Treatment of carboxylic acids with Grignard reagents gives only a half-way result, and it has not been found possible to obtain from them any new product. The initial reaction with one molecule of a Grignard reagent no doubt yields a magnesio-halide salt and an alkane,



$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{OH}} + \mathrm{C_2H_5MgBr} \rightarrow \mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{OMgBr}} + \mathrm{C_2H_6},$$

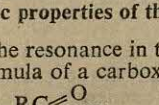
but the salt refuses to react further with a second molecule of Grignard reagent, and the decomposition of the magnesio-halide salt gives nothing but the original acid :



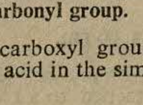
$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{OMgBr}} \xrightarrow{\mathrm{HOH}} \mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{OH}} + \mathrm{MgBr(OH)}$$

Resonance in the Carboxyl Group.—

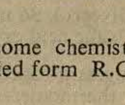
The comparative inertness of the carboxyl group referred to above is attributed to the existence of resonance. The physical evidence for this is furnished by X-ray diffraction measurements on acetates and other salts of carboxylic acids. These measurements show that *there is the same bond length between the carbon and both the oxygen atoms*, the value being *intermediate* between those for single and double carbon-oxygen links. Further, the unit negative charge of the ion is distributed *equally* between the two oxygen atoms. There is no satisfactory way of representing this state of affairs by a single formula. Hence, the carboxylate ion is assigned the hybrid structure, the mesomeric form (I) being symmetrically related to the two contributing structures (II) and (III) given below :—



(I)



(II)



(III)

Because of the resonance, the double bond character of the carbon-oxygen link is considerably reduced. It is for this reason that the **carboxylic acids do not show the characteristic properties of the carbonyl group.**

Because of the resonance in the carboxyl group, some chemists now prefer to write the formula of a carboxylic acid in the simplified form $\mathrm{R.CO_2H}$, instead of the old form, $\mathrm{RC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{OH}}$.

9. Formic Acid, *Methanoic Acid*, HCOOH. This acid occurs in ants (L. *formica*), stinging nettles, bees and wasps, and also in perspiration, urine and the juice of flesh.

Laboratory Preparation. Formic acid is best prepared in the laboratory by heating oxalic acid crystals with an equal weight of anhydrous glycerol in a flask connected to a condenser and receiver

(Fig. 5). The temperature is maintained at 110°C, until the evolution of carbon dioxide slackens. The contents of the flask are then allowed to cool somewhat, a further quantity of oxalic acid crystals is added, and the heating renewed, when an aqueous solution of formic acid distils over.

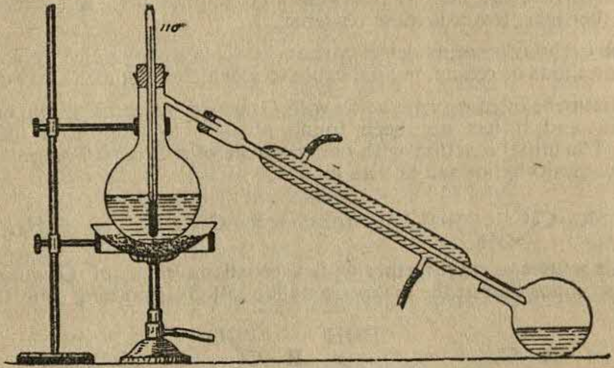
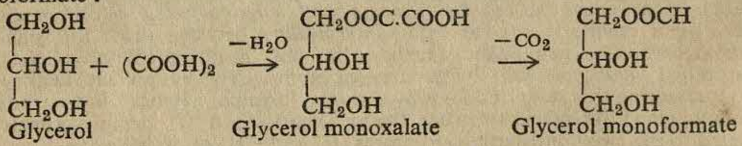


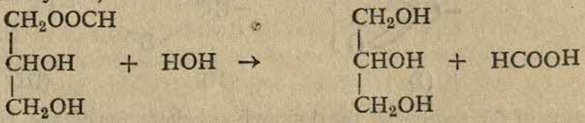
Fig. 5. Preparation of Formic Acid from Oxalic Acid.

Mechanism of the Reaction. It has been shown by Chattaway that during the first stage of the reaction, the primary oxalic ester of glycerol is formed, which, with the rise of temperature, loses a molecule of carbon dioxide yielding glycerol monoformate :



$$\begin{array}{lcl}
\begin{array}{l} CH_2OH \\ | \\ CHOH + (COOH)_2 \\ | \\ CH_2OH \\ \text{Glycerol} \end{array}
& \xrightarrow{-H_2O} &
\begin{array}{l} CH_2OOC.COOH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol monoxalate} \end{array}
\xrightarrow{-CO_2}
\begin{array}{l} CH_2OOCH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol monoformate} \end{array}
\end{array}$$

In the second stage, when more of oxalic acid crystals are added and the mixture reheated, glycerol monformate is hydrolysed by the water of crystallization present in oxalic acid crystals, and formic acid is set free :



$$\begin{array}{l} CH_2OOCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HOH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HCOOH$$

Expt. 1. *Preparation of Formic Acid* :—

Glycerol, 36 ml.
Oxalic acid crystals, 60 gm.

Place the glycerol together with one-half (30 gm.) of the oxalic acid in a flask fitted with a thermometer attached to a Liebig condenser. Heat the flask on a sand-bath to a temperature of 110°. A vigorous evolution of carbon dioxide occurs. When it slackens allow the mixture to cool somewhat, add the remainder of the oxalic acid and repeat the heating at 110°. The evolution of carbon dioxide will begin afresh, and, at the same time, aqueous formic acid will distil over.

Use the distillate obtained in the experiment for studying the reactions of formic acid (Expt. 2, p. 310).

Anhydrous Formic Acid. The aqueous solution of formic acid, obtained as above, is neutralized with litharge, and then evaporated to get crystals of lead formate. After being dried, the lead salt is decomposed with hydrogen sulphide at 100°, when anhydrous formic acid is obtained. This may be purified further by distilling over lead formate, which removes hydrogen sulphide.

Manufacture. Formic acid is manufactured by passing carbon monoxide at a pressure of eight atmospheres over soda-lime heated at 200°. The reaction is quantitative :

$$CO + NaOH \rightarrow \underset{\text{Sodium formate}}{HCOONa}$$

The resulting sodium formate is distilled with sodium hydrogen sulphate, when anhydrous formic acid passes over :

$$HCOONa + NaHSO_4 \rightarrow HCOOH + Na_2SO_4$$

Properties. Anhydrous formic acid is a colourless liquid, possessing a penetrating pungent odour, and boiling at 100·6°. It is strongly corrosive, and raises blisters on the skin. It is perfectly miscible with water, alcohol, ether and many other solvents.

As already mentioned (Sec. 5), formic acid exhibits **association**, the vapour density determination indicates that the vapour is a mixture of single and double molecules.

The acid forms a constant-boiling mixture with water that boils *higher* than either component. It contains 22·5 per cent water, and boils at 107°.

The reactions of formic acid, HCOOH, are due to (*a*) the carboxyl group, and (*b*) the hydrogen atom directly linked to the carboxyl group.

(1) The reactions of the carboxyl group have already been discussed (sec. 6). Formic acid is much stronger than acetic acid or any other member of this series. It forms water-soluble salts ; those of lead and copper crystallize particularly well.

(2) Because of the hydrogen atom linked to the carboxyl group, formic acid, like the aldehydes, is an **active reducing agent.** It decolorizes permanganates, reduces ammoniacal silver nitrate to metallic silver (black precipitate or silver mirror) and the mercuric salts to mercurous salts or metallic mercury.

The reducing action of formic acid is utilized in a method (Fulmer, 1931) for the **separation of copper and cadmium** in analysis. The solution is mixed with potassium formate evaporated and heated at 160°. The cupric ion gets reduced to metallic copper, while the cadmium salt is left unaffected.

Formic acid is also employed in **certain organic reductions,** for example, reduction of carboxylic acids to aldehydes and of triphenylcarbinol to triphenylmethane.

(3) Formic acid is capable of undergoing decomposition in two different ways :

$$(i)\ HCOOH \rightarrow H_2O + CO$$

$$(ii)\ HCOOH \rightarrow H_2 + CO_2$$

The decomposition (*i*) is brought about by warming the acid with concentrated sulphuric acid, or by passing its vapour over heated alumina. Finely-divided copper, nickel and certain other catalysts bring about the decomposition (*ii*).

Expt. 2. *Detection of Formic Acid.* In order to apply the following tests, the acid must first be exactly neutralised with sodium carbonate and a few drops of ammonia, the excess of the latter being boiled off. A part of the solution should be evaporated to dryness to get the solid formate.

(1) *Action of Heat.* On heating the sodium salt, hydrogen is set free and the residue gives the tests of an oxalate :

$$2HCOONa \rightarrow Na_2C_2O_4 + H_2$$

(2) When the dry salt is heated with *dilute sulphuric acid,* pungent, penetrating odour of formic acid is observed.

(3) On heating with *concentrated sulphuric acid,* carbon monoxide is evolved, which may be ignited at the mouth of the test-tube (distinction from acetic acid).

(4) When a solid formate is heated with *alcohol and concentrated sulphuric acid,* a pleasant fruity odour of ethyl formate is developed.

(5) *Ferric chloride,* when added to a neutral solution of a formate, gives a red coloration, owing to the formation of ferric formate. On heating the solution a reddish brown precipitate of a basic ferric formate is produced (compare acetic acid).

(6) *Silver nitrate,* when added to a neutral concentrated solution of a formate, gives a white crystalline precipitate of silver formate. On standing, the precipitate darkens owing to its reduction to metallic silver. In dilute solution, there occurs no precipitation ; but on warming separation of metallic silver takes place (distinction from acetic acid).

(7) When *mercuric chloride* is added to a neutral solution of a formate, and the liquid warmed, a white precipitate of mercurous chloride is produced ; on further heating, reduction to metallic mercury occurs (distinction from acetic acid).

Constitution. The constitution of formic acid, $\mathrm{H.C}{<}^{\mathrm{O}}_{\mathrm{OH}}$, follows from its synthesis from hydrogen cyanide, $H.C{\equiv}N$. This view is fully supported by—

(1) the formation of the acid by the hydrolysis of chloroform, $CHCl_3$,

(2) the various reactions of the acid, described above.

Industrial Uses of Formic Acid.—

Formic acid being a cheap acid and, as compared with most other organic acids, a strong one, finds much use in various industries :—

(1) It is employed on a large scale in the textile industry for the preparation of mordants and for the dyeing of cotton and wool from an acid bath.

(2) It is used in the leather industry for removing lime from the hides.

(3) Another use of formic acid is in electroplating ; it helps in the proper deposit of metals.

(4) Antiseptic properties of formic acid are utilized in the brewing industry and in the preserving of fruit juices, etc.

10. Acetic Acid, *Ethanoic Acid,* CH_3COOH.—This is the most common organic acid and the one longest known. In fact, dilute acetic acid, in the form of vinegar, was the only acid known to the ancients.

Manufacture of Acetic Acid. There are at present four different methods for the production of acetic acid on the commercial scale :—

(1) **Fermentation Process.** The oldest method for the production of acetic acid is the acetous fermentation of ethyl alcohol in dilute solution. Edible acetic acid, or **vinegar**, is required by law to be made only by the fermentation process, otherwise it cannot be labelled as '*vinegar*'. Vinegar contains from 4 to 6 per cent of acetic acid, and is prepared by fermenting various solutions containing sugars. The name of the vinegar indicates the source. Thus, we have **wine vinegar** (from grapes), **cider vinegar** (from apples), **malt vinegar** (from barley), and **white vinegar** (from dilute alcohol). Besides acetic acid and water, vinegar contains other substances (such as esters, salts, colouring matters, etc.) derived from the original source.

The fermentation of fruit juices to produce vinegar consists of two separate processes, which proceed one after the other. Yeasts first convert the sugars present into ethyl alcohol, and the alcohol is then oxidised to acetic acid by air in the presence of **Acetobacters** or **acetic acid bacteria.** Both the yeasts and the Acetobacters are present on the skins of the fruits used.

The reaction, by which alcohol is converted to acetic acid,

$$2C_2H_5OH + 2O_2 \longrightarrow 2CH_3COOH + 2H_2O$$

is **exothermic.** As the oxidation is carried out through bacterial action, the temperature must be kept low enough for favourable action of the bacteria. This is brought about by allowing the dilute alcoholic solution to trickle *slowly* down the apparatus to allow the heat to be dissipated. Alternatively, the liquid is circulated rapidly with special arrangement for cooling during the circulation.

In the old "**cask method**" for the preparation of vinegar, wooden vats (Fig. 6) are filled with beechwood shavings moistened with strong vinegar containing bacterium aceti. Dilute alcohol (6 to 10 per cent) is allowed to flow slowly through the vats. The shavings serve firstly to present a large liquid surface to the oxidizing action of air, and secondly, they provide a suitable feeding ground for the acetic acid bacteria. Each vat is provided with a perforated top, *T*, and a perforated false bottom, *B*. Holes, *H*, in the sides of the vat near the bottom serve to admit an ascending current of the air, opposite in direction to the flow of the liquid. The process is repeated several times to complete the oxidation, which requires about a fortnight.

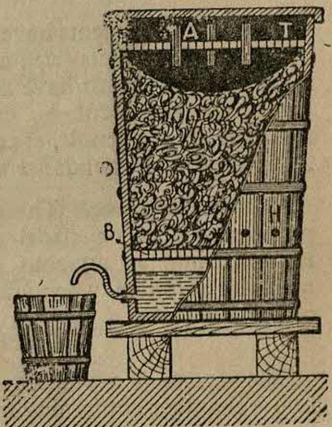


Fig. 6. The "cask method" for the production of vinegar.

In the modern method, called the **quick vinegar process** or the **generator process**, pure yeast cultures are used to bring about the alcoholic fermentation of fruit juices. The alcoholic liquor, thus obtained, is mixed with vinegar from previous operation, and the mixture allowed to trickle down tall wooden towers (20 feet high and 10 feet in diameter) packed with beechwood shavings and provided with false bottoms. A counter-current of air passes up the towers, and, through the agency of an enzyme secreted by the bacteria, brings about the oxidation of alcohol. The process takes about a week to complete, and the yield is about 15 gallons of 10 per cent vinegar per day.

(2) **Catalytic Vapour-Phase Oxidation of Ethyl Alcohol.** In this important method, a mixture of air and ethyl alcohol vapour is passed over a heated catalyst, when ethyl alcohol gets directly oxidized to acetic acid.

(3) **Wood Distillation Process.** Acetic acid is recovered as an important product from the **pyroligneous acid** obtained in the destructive distillation of wood (p. 237). The old method of separation consisted in neutralizing the acidic liquid with lime so as to produce calcium acetate. The volatile components were distilled off, the water evaporated and the residual dry salt distilled with sulphuric acid to recover acetic acid.

On account of competition from synthetic processes, the methods for the separation of acetic acid and other components from pyroligneous acid have been considerably improved. They include (*i*) Continuous and systematic **extraction with solvents**, such as ethyl ether, isopropyl ether and an oil extracted from pyroligneous acid itself, and (*ii*) **azeotropic distillation** based on the same principle as described in the case of Absolute Alcohol (p. 243).

These improvements have not only lowered the cost of production of the chief products (*viz.*, acetic acid, methyl alcohol and acetone) from wood, but also have added a multitude of by-products, such as acids, acetals, alcohols, ethers, aldehydes, esters, amines, furans, hydrocarbons, phenols, *etc.*, totalling nearly 200 compounds. About 20 of these compounds are already on the market for sale.

(3) **From Acetylene.** The cheapest method for the production of pure acetic acid, or **glacial acetic acid**, is from acetylene. The gas is passed into an aqueous solution containing sulphuric acid and mercuric sulphate, when addition of water occurs with the production of acetaldehyde :

$$HC{\equiv}CH + H_2O \rightarrow CH_3.CHO$$

The vapour of acetaldehyde is mixed with air and the mixture led into a chamber containing manganese acetate wet with acetic acid and heated at 70°, when acetaldehyde gets oxidized to acetic acid.

$$CH_3CHO + O \rightarrow CH_3COOH$$

11. Properties of Acetic Acid.—Acetic acid is a colourless liquid, having a very strong, pungent odour and a corrosive action on the skin. In cold weather, the acid freezes to give a transparent, crystalline mass (m.p. 16·6°). Hence the name **Glacial Acetic Acid** given to the anhydrous acid. The pure acid boils at 118°, and is heavier than water.

When water is the only impurity present in acetic acid, its amount can be readily determined by noting the freezing point, which is lowered by 2·16° for one per cent of water[1] present.

Acetic acid possesses the usual reactions of this series (sec. 6).

Expt. 3. Detection of Acetic Acid and Acetates. The free acid may be identified by its characteristic, pungent smell. For the following tests, prepare a *neutral* solution, as in the case of formic acid and evaporate a part of it to get solid sodium acetate.

(1) Heat the dry sodium salt in a test tube; no gas is evolved (distinction from formic acid).

(2) Heat the dry salt with sulphuric acid (dilute or concentrated); pungent smelling vapour of the acid is evolved.

(3) Heat the dry salt with amyl alcohol and concentrated sulphuric acid; a fruity odour of amyl acetate is developed.

(4) Add ferric chloride to the *neutral* solution; a deep red coloration is produced, owing to the formation of ferric acetate. The colour is discharged on boiling the liquid, a brownish red precipitate of basic ferric acetate being deposited. The liquid also gets decolorized on the addition of hydrochloric acid, owing to the decomposition of ferric acetate.

12. Uses of Acetic Acid :—(1) In the form of vinegar, acetic acid is much used as a condiment and for pickling.

(2) In the laboratory, the acid is used as a reagent and as a solvent.

(3) Large quantities of this acid are used in the manufacture of dyes, rayon and paper.

(4) It is also employed on a large scale in the manufacture of ethyl acetate, amyl acetate and other esters for use as solvents in the lacquer industry.

(5) Certain metallic acetates (*e.g.*, lead, copper, aluminium and iron) are used on a very large scale (*see* sec. 13).

13. Acetates.—All normal acetates are soluble in water; some basic acetates are insoluble.

Sodium Acetate, $CH_3COONa.3H_2O$, is used for artificial cooling and as a reagent.

Lead Acetate, or **sugar of lead**, $(CH_3COO)_2Pb, 3H_2O$, and **basic lead acetate**, $CH_3COOPb(OH)$, are used in the manufacture of lead preparations (*e.g.*, "white lead"). A solution of lead acetate in water is sometimes used under the name "lead lotion" as an external application in cases of sprains, etc.

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[1] The figure 2·16 is calculated from the molecular depression constant of acetic acid, which is 38·8°.

Basic copper acetate, $CH_3COOCu(OH)$, technically known as **verdigris**, is used in the manufacture of green paint. Normal acetates of *aluminium chromium*, *iron* and *copper* are largely employed as mordants.

14. Propionic Acid.— CH_3CH_2COOH. This acid is now prepared by the direct addition of carbon monoxide and ethyl alcohol under pressure in the presence of BF_3 as the catalyst. It may also be obtained by the oxidation of propyl alcohol with potassium dichromate and sulphuric acid. It boils at 141°, and mixes with water in all proportions. From the aqueous solution, however, it can be "salted out" as an oily layer by the addition of solid calcium chloride and other salts.

Sodium propionate and **calcium propionate** are commercially available, and are employed to prevent the growth of mold and fungus in baked goods and other vegetable materials including tobacco.

15. Butyric Acids, C_3H_7COOH.—There are two isomeric butyric acids, both of which are found in nature :

(1) ***n*-Butyric Acid**, *Ethylacetic Acid*, $CH_3CH_2CH_2COOH$. This acid occurs as the glyceryl ester in butter to the extent of about 7 per cent, and in the free state in perspiration.

The acid is prepared by the **butyric fermentation** of saccharine or starchy materials, which is brought about by the combined action of the *lactic bacilli* and the *butyric bacilli*.

A solution of starch or glucose is prepared and to this some sour milk (which contains lactic ferment) and putrid cheese (which contains butyric ferment) are added. Some chalk or zinc carbonate is also added to keep down the hydrion concentration of the fermenting liquid (as excessive acidity is ruinous to the growth of the ferments) and also a little tartaric acid, ammonium phosphate, and magnesium sulphate, in order to stimulate the growth of the ferments. The butyric acid, as soon as produced, gets neutralized by the calcium or zinc carbonate present. The resulting solution, containing calcium or zinc butyrate is filtered, evaporated, decomposed with hydrochloric acid, and butyric acid separated by distillation.

During the above process of fermentation, the starch is first converted into glucose. The latter then undergoes lactic fermentation. Finally, the lactic acid is decomposed to give butyric acid :—

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Lactic acid}}{2C_3H_6O_3} \rightarrow \underset{\text{Butyric acid}}{C_4H_8O_2} + 2CO_2 + 2H_2$$

n-Butyric acid is an oily liquid (b.p. 163°), having an unpleasant smell of rancid butter. It is used in the manufacture of esters.

The **calcium salt of *n*-butyric acid** shows the peculiar behaviour of being *less* soluble in hot water than in the cold. This fact is utilized for distinguishing the normal butyric acid from isobutyric acid, the calcium salt of the latter behaving normally, *i.e.*, it is more soluble in hot water than in the cold.

(2) **Isobutyric Acid**, *Dimethylacetic Acid*, $(CH_3)_2CH.COOH$. This acid is found in the free state, or as esters, in many plants. It is prepared by the oxidation of isobutyl alcohol, $(CH_3)_2CH.CH_2OH$.

It is an oily liquid, boiling at 154°. It differs from the normal acid in being immiscible with water and in the solubility of the calcium salt in hot water.

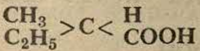
16. Valeric Acids.—All the four C_5-acids of this series required by theory are known, and are collectively called "*valeric acids*".

***n*-Valeric Acid**, *Pentanoic Acid*, $CH_3(CH_2)_3COOH$. This acid is found in small quantities in pyroligneous acid. It may be prepared by the oxidation of 1-pentanol or from 1-butanol through the bromide and the cyanide. It is also obtained from levulinic acid (got by hydrolysis of sucrose with hydrochloric acid) by reduction with sodium amalgam :

$$\underset{\text{levulinic acid (}\gamma\text{-ketopentanoic acid)}}{CH_3COCH_2CH_2COOH} \rightarrow \underset{n\text{-valeric acid}}{CH_3CH_2CH_2CH_2COOH}$$

Isovaleric Acid, *3-Methylbutanoic acid, isopropylacetic acid*, $(CH_3)_2CHCH_2COOH$, is found in the free state in valerian root, from which it can be extracted by steam distillation. The acid thus obtained is used in certain medicinal preparations, which exhibit slight optical activity due to the presence of small quantities of active valeric acid.

Active Valeric Acid, *2-Methylbutanoic acid, Methylethylacetic acid.*—Since the molecule of this acid contains an asymmetric carbon atom, the acid shows optical activity and occurs as the *d*-form, the *l*-form, and the inactive "racemic mixture" containing equal quantities of the two active forms. When prepared by oxidation of *d*-amyl alcohol from fusel oil, the product is dextro-rotatory. On the other hand, when prepared synthetically from inactive materials, say by the malonic ester or acetoacetic ester synthesis, the product is optically inactive due to external compensation. The resolution of this "racemic mixture" into the *d*- and the *l*-forms can be effected by salt formation with *d*-brucine.



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\COOH\end{matrix}$$

Trimethylacetic acid, $(CH_3)_3C.COOH$, may be obtained by the hydrolysis of tertiary butyl cyanide, $(CH_3)_3C.CN$. It gives the usual acid reactions, which, however, are modified on account of the accumulation of alkyl group on the *alpha*-carbon. Thus, its rate of esterification is much lower than that of isobutyric acid, $(CH_3)_2CH.COOH$.

17. Higher Homologues.—Some higher members of the series having a normal chain and an even number of carbon atoms are found as glyceryl esters in fats and oils of animals and vegetable origin. Two of these *viz.*, **palmitic acid**, $C_{15}H_{31}COOH$, melting at 62°, and **stearic acid**, $C_{17}H_{35}COOH$, melting at 69°, are the most important. A mixture of the two acids is manufactured on a large scale by hydrolysing fats, and is used in the manufacture of "stearine" candles. Soap is a mixture of the sodium salts of these acids.

II. UNSATURATED MONOCARBOXYLIC ACIDS

18. Oleic Acid Series.—The monocarboxylic acids derived from olefin hydrocarbons have the general formula $C_nH_{2n-1}COOH$. The most important member of the series is oleic acid, from which the series takes its name.

19. General Methods of Formation.—The acids of the oleic series may be obtained by methods analogous to those used in the case of fatty acids (Sec. 4), and also by the general methods for the preparation of unsaturated compounds. The following are the chief methods used for the purpose :—

(1) By oxidizing the corresponding primary alcohols or aldehydes; *e.g.*,

$$\underset{\text{Allyl alcohol}}{CH_2{=}CH.CH_2OH} \rightarrow \underset{\text{Acrylic aldehyde}}{CH_2{=}CH.CHO} \rightarrow \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

(2) From the olefin alcohols or their iodides, by converting them into the nitriles, which are then hydrolysed. Starting with allyl alcohol, we expect to obtain 3-butenoic acid as shown below :

$$\underset{\text{Allyl alcohol}}{CH_2{=}CH.CH_2OH} \xrightarrow{HI} \underset{\text{Allyl iodide}}{CH_2{=}CH.CH_2I} \xrightarrow{KCN}$$

$$\underset{\text{Allyl cyanide}}{CH_2{=}CH.CH_2.CN} \xrightarrow{\text{Hydrolysis}} \underset{\text{3-Butenoic acid}}{CH_2{=}CH.CH_2.COOH}$$

Actually, however, we get an isomeric acid, called **crotonic acid** (2-butenoic acid), by intramolecular rearrangement :

$$CH_2{=}CH.CH_2COOH \rightarrow \underset{\text{Crotonic acid}}{CH_3.CH{=}CH.COOH}$$

(3) By the removal of halogen hydride from monohalogen substitution products of fatty acids containing the halogen in the β-position to the carboxyl. The reaction may be effected sometimes by simply heating the halogenated acid with water :

$$\underset{\beta\text{-Chloro-propionic acid}}{CH_2Cl.CH_2.COOH} \xrightarrow{-HCl} \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

(4) By the removal of the elements of water from a β-hydroxy acid (which can be effected by simply heating the hydroxy acid) :—

$$\underset{\beta\text{-Hydroxypropionic acid}}{CH_2(OH).CH_2.COOH} \xrightarrow{-H_2O} \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

(5) **Knoevenagel Reaction.**—This is a general method for the preparation of alpha-beta-unsaturated monocarboxylic acids, and consists in treating an aldehyde with malonic acid in the presence of pyridine (catalyst). The unsaturated malonic acid derivative, first formed, undergoes decarboxylation during condensation, with steady evolution of carbon dioxide. Thus, acetaldehyde gives crotonic acid :

$$CH_3CH\boxed{O + H_2}C(COOH)_2 \xrightarrow[-H_2O]{\text{pyridine}} CH_3CH{=}C(COOH)_2$$

$$\xrightarrow{-CO_2} CH_3CH{=}CHCOOH$$

20. Physical Properties of Unsaturated Monocarboxylic Acids.— Apart from differences in melting point, which are sometimes considerable, the physical properties of the acids of the oleic series are similar to those of the fatty acids. The presence of the double bond increases the strength of the acid, the effect being maximum when the double bond occupies the β, γ-position.

21. Chemical Properties of Unsaturated Monocarboxylic Acids.— The acids of the oleic series have two sets of reactions. Firstly, like the fatty acids, they possess the properties of the carboxyl group. Secondly, they show the reactions characteristic of the double bond. With respect to the first, nothing particular need be mentioned, except that, as already stated, the presence of the double bond makes them stronger acids than those of the fatty series. In connection with the second, the following points may be mentioned :

(1) They can be converted into the corresponding saturated acids by catalytic reduction (hydrogenation). The hydrogenation of the glyceryl ester of oleic acid is of great practical importance, and is used in the hardening of fats and oils.

(2) They combine, as usual, with chlorine, bromine and iodine, yielding dihalogen derivatives of the corresponding saturated acids, *e.g.*,

$$\underset{\text{Acrylic acid}}{CH_2{=}CH.COOH} + Cl_2 \rightarrow \underset{\text{2,3-Dichloropropionic acid}}{CH_2Cl.CHCl.COOH}$$

The addition of halogen hydrides to the acids of this series occurs quantitatively in a sense opposed to Markownikoff's rule. Thus, acrylic acid gives with hydriodic acid, *beta*-iodopropionic acid :—

$$\underset{\text{Acrylic acid}}{H_2C{=}CHCOOH} + HI \longrightarrow \underset{\beta\text{-iodopropionic acid}}{CH_2I.CH_2COOH}$$

(3) The acids of this series, like the olefins themselves, unite with ozone to form unstable ozonides. The decomposition of these by water affords an excellent method for determining the position of the double bond in the molecule.

(4) The unsaturated acids readily undergo *oxidation*. With a mild oxidizing agent (*e.g.*, 1 per cent $KMnO_4$) two hydroxyl groups are added as in the case of ethylene :

$$\underset{\text{Crotonic acid}}{CH_3.CH{=}CHCOOH} + H_2O + O \rightarrow \underset{\alpha,\beta\text{-Dihydroxybutyric acid}}{CH_3.CH(OH).CH(OH).COOH}$$

But, if a stronger oxidizing agent be used, the oxidation proceeds further, each of the —CHOH groups being oxidized to a carboxyl group. Thus there occurs a rupture of the molecule at the position of the double bond, two molecules of saturated acids being thereby formed :

$$\underset{\alpha,\beta\text{-Dihydroxybutyric acid}}{CH_3.CHOH.CHOH.COOH} + 3O \rightarrow \underset{\text{Acetic acid}}{CH_3.COOH} + \underset{\text{Oxalic acid}}{COOH.COOH} + H_2O$$

The reaction affords another means of determining the position of **the double bond in the molecule.**

(5) A rupture of the molecule with the formation of saturated acids also occurs on fusion with alkalis in the presence of air :

$$\underset{\text{Crotonic acid}}{CH_3CH=CH.COOH} + H_2O + O \rightarrow \underset{\text{Acetic acid (2 molecules)}}{CH_3.COOH + CH_3COOH}$$

The reaction, however, is of no use for locating the position of the double bond, as treatment with alkali has been shown to shift the double bond, if possible, nearer to the carboxyl.

A similar shifting of position of double bond is also sometimes observed, when an unsaturated cyanide is subjected to hydrolysis (compare, for example, the conversion of allyl cyanide into crotonic acid, p. 316).

22. Constitution of Unsaturated Acids.—The determination of the constitution of an unsaturated acid involves the following points :

(*i*) The *nature of the chain.* This point is settled by hydrogenating the acid to the corresponding saturated acid.

(*ii*) The *position of the double bond* in the molecule. This is done by oxidizing the acid, or by ozonolysis.

23. Acrylic Acid, *Propenoic Acid*, $H_2C=CH.COOH$. This acid is best prepared from ethylene chlorohydrin as follows :

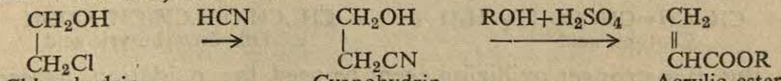
$$\underset{\text{Ethylene chlorohydrin}}{CH_2OH.CH_2Cl} \xrightarrow{KCN} \underset{\text{β-Hydroxypropionitrile}}{CH_2OH.CH_2CN} \xrightarrow{HOH}$$

$$\underset{\substack{\text{β-Hydroxypropionic acid} \\ \text{(Hydracylic acid)}}}{CH_2OH.CH_2COOH} \xrightarrow{-H_2O} \underset{\text{Acrylic acid}}{CH_2=CHCOOH}$$

It is a liquid having a pungent odour, resembling that of acetic acid. It melts at 12·3° and boils at 140°. It shows all the reactions characteristic of this series (p. 317).

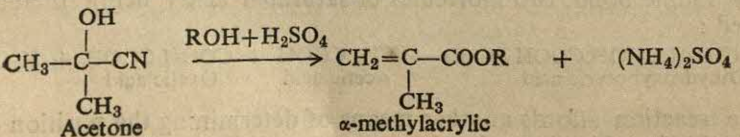
24. Acryloid Plastics.—Acrylic esters, $CH_2=CH.COOR$, and *alpha*-methylacrylic esters, $CH_2=C(CH_3).COOR$, polymerize readily under the influence of heat, light, oxygen, or peroxides. The products, called **acryloids,** are colourless and transparent resins, possessing excellent optical properties, and can be moulded into lenses, prisms and sheets for making laminated safety glass.

The **acrylic esters** used in the manufacture of acryloid plastics are industrially prepared from ethylene chlorohydrin (readily available from Petroleum) as follows :



$$\underset{\text{Chlorohydrin}}{\begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array}} \xrightarrow{HCN} \underset{\text{Cyanohydrin}}{\begin{array}{l} CH_2OH \\ | \\ CH_2CN \end{array}} \xrightarrow{ROH+H_2SO_4} \underset{\text{Acrylic ester}}{\begin{array}{l} CH_2 \\ \| \\ CHCOOR \end{array}}$$

Alpha-methylacrylic esters are prepared from acetone cyanohydrin by simultaneous esterification and dehydration :



$$\underset{\substack{\textbf{Acetone} \\ \textbf{cyanohydrin}}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CN} \xrightarrow{ROH+H_2SO_4} \underset{\substack{\textbf{α-methylacrylic} \\ \textbf{ester}}}{CH_2=\underset{\underset{\displaystyle CH_3}{|}}{C}-COOR} + (NH_4)_2SO_4$$

Acryloid plastics are available under several trade names some of which, together with their uses, are given in the following table.

Name	Use
Acryloic	for coatings
Plexigum	for laminated glass binders
Plexiglass	Transparent sheets
Lucite	Sheets and moulding compounds
Crystallite	Moulding compounds

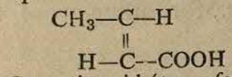
The first two of the above list are obtained from acrylic esters and the rest from *alpha*-methylacrylic esters.

25. Crotonic and Isocrotonic Acids : *2-Butenoic acids,* $CH_3.CH=CH.COOH$.—

Ordinary **crotonic acid** or *solid crotonic acid* occurs in croton oil, and resembles acrylic acid closely. It may be obtained by the general methods, given above, or by the hydrolysis of allyl cyanide. It melts at 72° and boils at 180°.

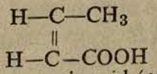
When solid crotonic acid in toluene solution is irradiated with ultra-violet light, it isomerizes into **isocrotonic acid**, which melts at 15° and boils at 169°. When heated at 170° to 180° in a sealed tube, it passes back into solid crotonic acid.

Crotonic and isocrotonic acids are structurally identical. On reduction they *both* yield normal butyric acid, showing that the molecules contain no branched chain. With dilute potassium permanganate, each of them yields dihydroxybutyric acid, while with nitric acid a mixture of acetic acid and oxalic acid is produced. This proves the constitution of the acids. Solid crotonic acid, because of its being chemically more stable, was assigned the *trans*-formula, while the less stable isocrotonic acid was assumed to be the *cis*-compound.



$$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-COOH \end{array}$$

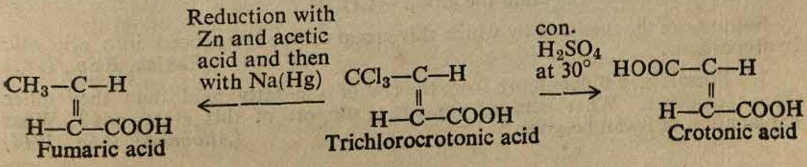
Crotonic acid (*trans-form*)



$$\begin{array}{c} H-C-CH_3 \\ \| \\ H-C-COOH \end{array}$$

Isocrotonic acid (*cis-form*)

Auwers, in 1923, proved this assumption to be correct by relating *crotonic* acid to *fumaric* acid by the preparation of each of these acids from a common intermediate by reactions which avoided all possibility of change of configuration :



$$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-COOH \end{array} \xleftarrow{\text{Reduction with Zn and acetic acid and then with Na(Hg)}} \begin{array}{c} CCl_3-C-H \\ \| \\ H-C-COOH \end{array} \xrightarrow{\text{con. } H_2SO_4 \text{ at } 30^\circ} \begin{array}{c} HOOC-C-H \\ \| \\ H-C-COOH \end{array}$$

Fumaric acid **Trichlorocrotonic acid** **Crotonic acid**

26. Oleic Acid, $CH_3.(CH_2)_7.CH=CH.(CH_2)_7.COOH$, *i.e.*, 9-*Octadecenoic acid*, is the most important member of the present series. It occurs as the glyceryl ester, *triolein*, in fatty oils (such as olive oil and cotton-seed oil), from which it is obtained as a by-product in the manufacture of stearine.

In the laboratory, oleic acid is best prepared from olive oil. The oil is saponified by boiling with an alkali solution. The water-soluble alkali salts of the acids present are then converted into insoluble lead salts by double decomposition with lead acetate. These are filtered, washed with alcohol to remove unchanged olive oil and then shaken with ether, which dissolves only the lead oleate, the lead salts of stearic and palmitic acids being insoluble in ether. The ethereal solution is filtered, the ether evaporated, and the residue of pure lead oleate decomposed with pure dilute nitric acid, when oleic acid is liberated as an oily layer. This is separated, dried with fused calcium chloride, and then distilled under reduced pressure.

Properties. Oleic acid is a colourless liquid, having practically no odour or taste. It solidifies at 4°, yielding a mass of colourless needles, which melt again when the temperature rises to 14°. In contact with air, the acid rapidly acquires a yellow colour and a sour rancid odour, owing to oxidation.

Constitution. When reduced, oleic acid yields stearic acid. Hence, like the latter compound, it must contain a *straight chain* of 18 carbon atoms. Further, on oxidation with cold, dilute potassium permanganate solution, it yields a mixture of *nonylic acid* and *azelaic acid* (nonanedioic acid). This shows that the double bond is in the middle of the chain:

$$\underset{\text{Oleic acid}}{CH_3.(CH_2)_7.CH=CH.(CH_2)_7COOH} \rightarrow$$

$$\underset{\text{Dihydroxystearic acid}}{CH_3.(CH_2)_7.CH(OH).CH(OH).(CH_2)_7.COOH} \rightarrow$$

$$\underset{\text{Nonylic acid}}{CH_3.(CH_2)_7.COOH} + \underset{\text{Azelaic acid}}{HOOC.(CH_2)_7.COOH}$$

When submitted to *ozonolysis*, the acid yields the following products:

$$\underset{\text{Nonylic aldehyde}}{CH_3(CH_2)_7CHO} \quad \text{and} \quad \underset{\text{Azelaic half-aldehyde}}{CHO.(CH_2)_7.COOH}$$

Uses. Oleic acid is used as a wool oil (*i.e.*, for oiling wool before spinning) and in soap manufacture.

QUESTIONS

1. What general methods are available for the preparation of carboxylic acids? Give an account of the more important reactions of these substances. (*Patna, B.Sc., 1953*)

2. On what grounds has the conclusion been drawn that the molecular formulae of fatty acids contain the group —COOH?

Summarize the methods by which this group can be introduced into aliphatic hydrocarbons. (*Punjab, B.Sc., 1942*)

3. Formic acid differs more from the rest of the fatty acid than they differ from each other. What facts can you cite in support of this statement? What explanation of it can be given? (*Allahabad, B.Sc., 1944*)

4. Discuss the constitution of Acetic Acid. *(Lucknow, B.Sc., 1959)*

5. How can acetic acid be prepared on a large scale? Give an outline of the reactions with the help of which acetic acid can be converted into (*a*) ethane, (*b*) acetone, (*c*) methane, and (*d*) acetaldehyde. *(Allahabad, B Sc., 1958)*

6. Starting from acetic acid, how would you prepare: (*a*) methane, (*b*) methylamine, (*c*) acetic anhydride, (*d*) acetone and (*e*) acetonitrile? Write equations. *(Gauhati, B Sc., 1958)*

7. An organic monobasic acid has the composition C, 40·0% and H, 6·67%. Its silver salt contains 54·8% silver. On oxidation with potassium dichromate and sulphuric acid it gives acetic acid, CH_3COOH. Deduce the structural formula of this acid and explain the formation of acetic acid from it. What happens if this acid is heated? *(Punjab, B.Sc., Chem. Engg., 1963)*

8. How is acetic acid manufactured? How will you obtain (*a*) methane; (*b*) ethane; (*c*) acetaldehyde; and (*d*) ethyl alcohol from it? *(Saugar, B. Sc., 1961)*

9. Starting from acetic acid, how may the following be obtained :—

(*a*) Acetyl chloride; (*b*) Acetic anhydride; (*c*) Acetamide; (*d*) Acetone? *(Bihar, B.Sc., 1961)*

10. Describe different methods for the preparation of saturated monocarboxylic acids. Describe their important properties, giving equations wherever necessary. *(Madras, B.Sc., 1962)*

11. How is formic acid obtained in a pure state? Give an account of its reactions.

How does it differ from acetic acid? *(Venkateswara, B.Sc., 1962)*

12. An acid, A, containing C, H and O only, gave on analysis C = 40·7%; H = 5·80%. The silver salt contained 65·8% silver. The acid on heating evolved CO_2, leaving a strongly acid liquid B. What is the probable constitution of the acid and that of the product formed on heating? *(Calcutta, B.Sc., 1951)*

Ans. $CH_3CH(COOH)_2$; CH_3CH_2COOH.

13. Indicate how propionic acid could be converted into :

(*a*) propionyl chloride, (*b*) propionic anhydride, (*c*) α-chloropropionic acid, (*d*) propionaldehyde, (*e*) lactic acid, (*f*) diethyl ketone, (*g*) *n*-butyric acid and (*h*) acetaldehyde. *(Agra, B.Sc., 1960)*

14. Starting from acetic acid how can you synthesise the following substances? Give the complete reactions in each case.

(*i*) Glycine; (*ii*) Lactic acid; (*iii*) Malonic acid; (*iv*) Acetylene; (*v*) Glycollic acid; (*vi*) Methylamine. *(Nagpur, B.Sc., 1960)*

15. (*a*) What are the general methods of obtaining carboxylic acids?

(*b*) State how acetic acid may be converted into (*i*) acetaldehyde, (*ii*) malonic acid, (*iii*) aminoacetic acid, (*iv*) nitromethane. *(Punjab, B.Sc., 1961)*

16. Two organic substances, *A* and *B*, had the same percentage composition. C = 40·0; H = 6·67%. The V. D. of *A* was 15 and that of *B* 30. *A* reduced Fehling's solution, but did not react with Na_2CO_3, while *B* did not reduce Fehling's solution but produced effervescence with Na_2CO_3 solution. Deduce the structural formulae of *A* and *B*.

Ans. (*A*) HCHO (*B*) CH_3COOH *(Delhi, B Sc., Hons., 1956)*

17. A monobasic organic acid gave on combustion C, 39·95 and H, 6·69 per cent. 0·2565 g. of the silver salt of the acid gave on ignition 0·1659 g. of silver.

Heating the sodium salt of the acid with soda lime gave a hydrocarbon. Distillation of the calcium salt of the acid gave a ketone which, on oxidation, gave the original acid. *[Bombay, B.Sc., Chemistry (Subs.), 1961)]*

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CHAPTER NINETEEN

DERIVATIVES OF MONOCARBOXYLIC ACIDS

1. General.—Derivatives of monocarboxylic acids are of two kinds (1) the derivatives formed by the substitution in the carboxyl group, and (2) those formed by substitution in the hydrocarbon radical. In this chapter, only the derivatives of class (1) are described ; the others will be discussed later.

1. ACID CHLORIDES

2. Nomenclature.—Acid chlorides, also called **acyl chlorides**, are derived from carboxylic acids by the replacement of the —OH component of the carboxyl group by a chlorine atom, and, consequently, contain the group $-\mathrm{C}{\lessgtr}^{\mathrm{O}}_{\mathrm{Cl}}$.

The common system of naming an acyl chloride is to replace the suffix **-ic** of the acid name by the class suffix **-yl**. Thus the chloride of *acetic* acid is named *acetyl* chloride and that of *n-butyric* acid *n-butyryl* chloride.

Similarly, in the I.U.C. system, the acid chlorides are named after the I.U.C. name of the acid. Thus, the chloride of *ethanoic* acid is called *ethanoyl* chloride and that of *n-butanoic* acid *n-butanoyl* chloride.

3. Preparation of Acid Chlorides :—

(1) *From Carboxylic Acids.* Acid chlorides are prepared from acids or their salts by the action of phosphorus pentachloride, phosphorus trichloride, or thionyl chloride :—

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$
$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$
$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

Of the above reagents, thionyl chloride is the best, as the by-products, being gases, escape and the acid chloride is left in the pure condition. The most commonly used reagent, however, is phosphorus trichloride, though it does not react quantitatively in accordance with the above equation. Much HCl is evolved on account of side reactions.

(2) *From Aldehydes.* Acid chlorides may also be prepared by the action of chlorine on anhydrous aldehydes in the *absence* of catalysts and sunlight :

$$RCHO + Cl_2 \rightarrow RCOCl + HCl$$

4. **Properties of Acid Chlorides.**—Acid chlorides are colourless, fuming liquids, possessing a sharp pungent odour.

Acid chlorides are very reactive substances and are employed for synthesizing several classes of compounds. Their more important reactions are :—

(1) They are readily attacked by water, yielding the parent acids and hydrogen chloride:

$$CH_3CO\vdots Cl + H\vdots OH \rightarrow CH_3COOH + HCl$$

(2) They react with alcohols and phenols, yielding esters :

$$CH_3CO\vdots Cl + H\vdots OC_2H_5 \rightarrow CH_3COOC_2H_5 + HCl$$

For this reason, acid chlorides (particularly acetyl chloride and benzoyl chloride) are employed for the detection and estimation of hydroxyl groups in organic compounds (see under Acetyl Chloride).

(3) They also act on ammonia and primary and secondary amines, yielding amides and alkyl amides :

$$CH_3COCl + \underset{\text{Ammonia}}{H.NH_2} \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

$$CH_3COCl + \underset{\text{Ethylamine}}{H.NHC_2H_5} \rightarrow \underset{\text{N-Ethylacetamide}}{CH_3CO\,NH(C_2H_5)} + HCl$$

$$CH_3COCl + \underset{\text{Diethylamine}}{H.N(C_2H_5)_2} \rightarrow \underset{\text{N-Diethylacetamide}}{CH_3CO.N(C_2H_5)_2} + HCl$$

In these reactions, an excess of ammonia or amine is used, and ammonium chloride or an amine hydrochloride is formed instead of hydrochloric acid as the by-product. The reactions are represented as above to bring out their analogy to the reactions of acetyl chloride with water and alcohol.

(4) In the presence of anhydrous aluminium chloride they react with the benzene hydrocarbons, yielding ketones (**Friedel and Crafts' reaction**) ; *e g.*,

$$CH_3COCl + \underset{\text{Benzene}}{C_6H_6} \rightarrow \underset{\text{Acetophenone}}{CH_3.CO.C_6H_5} + HCl$$

(5) They react with zinc alkyls and alkylmagnesium halides, yielding ketones (see pages 217 and 221).

(6) They react with sodium salts of carboxylic acids, yielding acid anhydrides ; *e.g.*,

$$\underset{\text{Acetyl chloride}}{CH_3CO\vdots Cl} + \underset{\text{Sodium acetate}}{Na\vdots OOC.CH_3} \rightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

(7) Lastly, they can be reduced to aldehydes through **Rosenmund's reaction** (p. 269) and to alcohols by lithium aluminium hydride p. 228).

5. **Formyl Chloride**, HCOCl, the first member of the series, is exceedingly unstable, and has not been isolated as such at ordinary temperatures. It has, however, been prepared at −170°, and is supposed to exist in equilibrium with CO and HCl :

$$CO + HCl \rightleftharpoons HCOCl$$

For this reason, a mixture of carbon monoxide and hydrogen chloride is employed to introduce the aldehyde group[1] into the aromatic nucleus. The reaction is carried out in the presence of anhydrous aluminium chloride (**Friedel and Crafts' reaction**), *e.g.*,

$$\underset{\text{Benzene}}{\mathrm{C_6H_6}} + \mathrm{HCOCl} \xrightarrow{\mathrm{AlCl_3}} \underset{\text{Benzaldehyde}}{\mathrm{C_6H_5CHO}} + \mathrm{HCl}$$

6. Acetyl Chloride, CH_3COCl.—Of the chlorides of aliphatic monocarboxylic acids, acetyl chloride is the most important, and is used in large amounts industrially and as a reagent in the laboratory.

Laboratory Preparation. In the laboratory, acetyl chloride is prepared by the action of phosphorus trichloride on glacial acetic acid.

Expt. 1. Preparation of Acetyl Chloride. 50 grams of glacial acetic acid are placed in a distillation flask, provided with a dropping funnel, a condenser, and a receiver (Fig. 1). The side-tube of the receiver is provided with a calcium chloride tube to keep out the moist air, 30 grams of phosphorus trichloride are gradually run from the dropping funnel into the distilling flask. During the addition of the trichloride, the flask is cooled by immersion in cold water contained in the water bath. The temperature of the bath is then raised to 40°—50° and kept at this point, until the evolution of hydrogen chloride has slackened, and the liquid in the flask has separated into two layers. The water of the bath is then boiled, until no more liquid collects in the receiver.

Purification. The acetyl chloride is purified by redistillation from the flask used as the receiver during the preparation, the neck of the flask being provided with a thermometer. The distillate is collected in another distillation flask, provided with a calcium chloride tube as before. The fraction passing between 53° and 56° is collected separately, and may be taken to be fairly pure for the

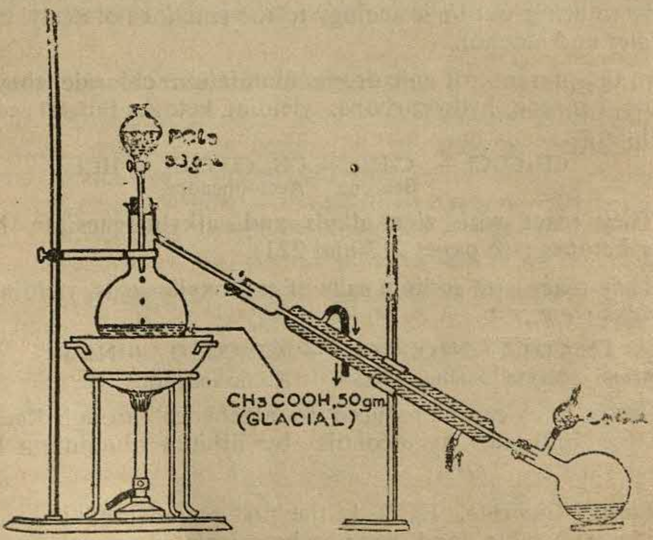

Fig. 1. Preparation of Acetyl Chloride.

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[1] As the aldehyde group is identical with the formyl group, the reaction may be called **"formylation"** (compare acetylation).

ordinary laboratory work. Further purification, if desired, can only be carried out by repeated fractional distillation.

Commercial Preparation of Acetyl Chloride. Acetyl chloride is prepared industrially by the action of a mixture of SO_2 and Cl_2 on sodium acetate :—

$$2CH_3COONa + SO_2 + Cl_2 \rightarrow 2CH_3COCl + Na_2SO_4$$

Properties of Acetyl Chloride. Acetyl chloride is a colourless, mobile liquid with a pungent odour. It boils at 55°.

7. **Acetyl Chloride as a Reagent.**—Acetyl chloride is an important **acetylating agent**, and is put to the following uses in the laboratory :—

(1) **Detection of the Hydroxyl Group.** Acetyl chloride is employed for detecting the presence of a hydroxyl group in the molecule of a compound. For this purpose, the substance, after being carefully dried, is added to an excess of acetyl chloride, the mixture is heated under a reflux condenser for some time, and the unchanged acetyl chloride is then distilled off. If the molecule contains no hydroxyl group, the substance under examination will be recovered unchanged. If, on the other hand, a hydroxyl group is present, an acetyl derivative of the substance will be formed :

$$\underset{\text{Hydroxy compound}}{ROH} + CH_3COCl \rightarrow \underset{\text{Acetyl derivative}}{ROCOCH_3} + HCl$$

The formation of acetyl derivative will be indicated by the evolution of HCl during the reaction, or the product may be boiled with alcoholic sodium hydroxide and the resulting solution tested for an acetate :

$$ROCOCH_3 + NaOH \rightarrow ROH + CH_3COONa$$

(2) **Determination of the Number of Hydroxyl Groups.** The determination of the number of hydroxyl groups in a compound consists in the preparation of the acetyl derivative, as described above, and then analysing the acetyl derivative for the number of acetyl groups that it contains.

If the acetyl derivative is that of a neutral compound (*e.g.*, a sugar), it is merely boiled with a known excess of standard alkali or acid, and the amount of acetic acid set free is determined by titration. In other cases, a known weight (about 0·2 gm) of the acetyl derivative is mixed with an excess of an aqueous solution of benzenesulphonic acid and the mixture distilled in steam, until acetic acid ceases to come over. The distillate is then titrated with a standard alkali.

(3) **As a Synthetic Agent.** Acetyl chloride is employed for synthesizing acetic anhydride, acetamide, substituted acetamides, ketones, *etc.*

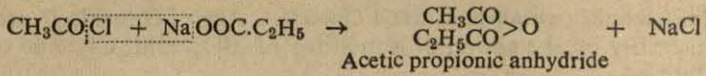
II. ACID ANHYDRIDES

8. **Preparation of Acid Anhydrides.**—(1) Acid anhydrides are prepared by the interaction of acid chlorides and the alkali salts of the acids ; *e.g.*,

$$\begin{matrix} CH_3CO\,Cl \\ + \\ CH_3COO\,Na \end{matrix} \rightarrow \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O + NaCl$$

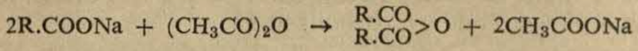
Acetic anhydride

If the two reacting substances are derived from different acids, a *mixed anhydride* is formed ; *e.g.*,



$$CH_3CO\overline{\underline{Cl + Na}}OOC.C_2H_5 \rightarrow \underset{\text{Acetic propionic anhydride}}{\begin{matrix}CH_3CO\\C_2H_5CO\end{matrix}\!>\!O} + NaCl$$

(2) The best method of preparing higher anhydrides consists in heating the sodium salts of the higher acids with acetic anhydride :



$$2R.COONa + (CH_3CO)_2O \rightarrow \begin{matrix}R.CO\\R.CO\end{matrix}\!>\!O + 2CH_3COONa$$

9. Properties of Acid Anhydrides.—The lower members of the series are colourless, non-fuming liquids, having a disagreeable and suffocating odour. The higher members are crystalline solids.

Acid anhydrides have a *neutral* reaction, and dissolve unchanged in different organic solvents. Like the acid chlorides, they act as **acetylating reagents** towards water, alcohols, ammonia and alkylamines. But they are far less vigorous reagents than the acid chlorides. The following reactions of acetic anhydride are typical of the series :—

$$\begin{array}{lrl}
 & CH_3CO\vdots O\,COCH_3 & \\
(1) & +HO\vdots H & \xrightarrow{\text{water}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetic acid}}{CH_3COOH} \\
(2) & +RO\vdots H & \xrightarrow{\text{alcohols}} \underset{\text{Alkyl acetate}}{CH_3COOR} + CH_3COOH \\
(3) & +NH_2\vdots H & \xrightarrow{\text{ammonia}} \underset{\text{Acetamide}}{CH_3CONH_2} + CH_3COOH \\
(4) & +RNH\vdots H & \xrightarrow{\text{amines}} \underset{\text{N-Alkyl acetamide}}{CH_3.CONHR} + CH_3COOH
\end{array}$$

In reactions (3) and (4), an excess of ammonia or amine is used, and ammonium acetate or an amine acetate is formed, instead of free acetic acid, as the by-product.

It is obvious that **only one of the two acetyl groups of acetic anhydride is used up during acetylation,** the other being eliminated as acetic acid.

10. Acetic Anhydride, $(CH_3CO)_2O$.—Acetic anhydride may be prepared in the laboratory by the interaction of anhydrous sodium acetate and acetyl chloride.

Expt. 2. Preparation of Acetic Anhydride.

Anhydrous sodium acetate, 50 gm.

Acetyl chloride, 30 ml.

Fit up the apparatus shown in Fig. 2, the side-tube of the receiver being connected to a calcium chloride tube to keep out atmospheric moisture. Place the anhydrous, finely powdered acetate in the retort, and drop slowly the acetyl chloride. When the whole of acetyl chloride has been added, remove the dropping funnel, stir the mixture well with a glass rod, and close the retort with a glass stopper. Heat the retort with a luminous flame, kept in constant motion.

When no more liquid collects in the receiver, add a little anhydrous sodium acetate to the collecting flask and redistil, collecting the fraction passing at 135° to 140°.

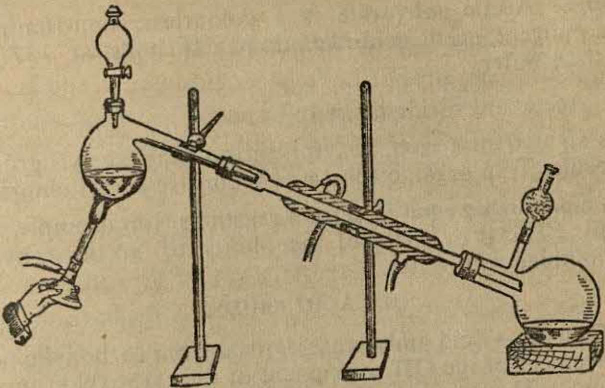


Fig. 2. Preparation of Acetic Anhydride.

Commercial Preparation. Acetic anhydride is of outstanding commercial importance, and is prepared on a large scale by two different methods.[1]

(1) **By addition of glacial acetic acid to ketene**[2] :

$$\begin{array}{c} CH_3.COO\vdots H \\ + \quad \vdots \\ OC=\vdots CH_2 \end{array} \rightarrow CH_3.CO—O—CO.CH_3$$

In this very important method ketene is produced by the pyrolysis of glacial acetic acid at high temperature in the presence of a liquid catalyst containing phosphoric acid,

$$CH_3COOH \rightarrow H_2C=CO + H_2O.$$

The ketene, thus produced, is made to pass up a column through which glacial acetic acid is flowing downwards.

(2) **By addition of glacial acetic acid (two molecules) to acetylene** : This reaction is carried out in the presence of mercuric salt, when **ethylidene acetate** is produced,

$$HC\equiv CH + 2CH_3COOH \rightarrow CH_3.CH(CH_3.COO)_2$$

---

[1] The former method of production from sodium acetate and acetyl chloride is no longer used as it is comparatively very uneconomical. The same is true of the modification in which sodium acetate was heated with S_2Cl_2 and chlorine.

[2] Ketene is an unsaturated ketone having the structure $H_2C=CO$. It is manufactured by rapidly passing acetone vapour through a chrome-iron tube heated at 650° (pyrolysis) :—

$$CH_3\vdots—CO—CH_2\vdots H \longrightarrow CH_4 + H_2C=C=O$$

Ketene is a colourless, highly poisonous gas with an exceedingly unpleasant odour. It is a powerful acetylating agent, and is commercially used in the production of acetic anhydride. In this case, ketene is produced by the pyrolysis of glacial acetic acid, and is used without being isolated.

The ethylidene acetate is distilled with zinc chloride, when it gets decomposed into acetic anhydride and acetaldehyde,

$$CH_3CH(CH_3COO)_2 \rightarrow CH_3CHO + (CH_3CO)_2O$$

Properties. Acetic anhydride is a colourless, non-fuming liquid having a pungent, acetic acid-like odour. It boils at 137°, and is heavier than water.

Uses. Acetic anhydride is used :—

(1) as an **acetylating agent**, *i.e.*, for introducing acetyl groups into the molecule of an organic substance (compare acetyl chloride) ;

(2) as a **dehydrating agent** in certain reactions (for example, Perkin's Reaction). This is by virtue of the ability of acetic anhydride to readily combine with water.

III. ACID AMIDES

11. General.—Acid amides are derived from carboxylic acids by the replacement of the OH component of the carboxyl group by the NH_2 group. They are named after the acids from which they are derived. Thus, the amides derived from formic and acetic acids are called *formamide* and *acetamide* respectively. In the I.U.C. system, the names are *methanamide* (from methanoic acid) and *ethanamide* (from ethanoic acid).

Amides may also be regarded as derived from ammonia by the replacement of the hydrogen of the ammonia molecule by acyl groups, when we get *primary*, *secondary* and *tertiary amides* (compare amines) :—

12. Preparation of Amides.—

(1) Amides may be obtained from ammonia by the action of acid chlorides (page 323), acid anhydrides (page 326), or esters. The reaction with acid chlorides is the one usually employed, but where this fails, an ester is used instead of the acid chloride. In this case, the reaction occurs as follows :

$$CH_3CO\vdots OR + H\vdots NH_2 \rightarrow CH_3CONH_2 + ROH$$

The ester is shaken with an equal volume of concentrated ammonia until it has dissolved[1]. The mixture is then fractionally distilled. Methyl esters are more readily converted into amides than their higher homologues.

(2) The amide of an acid can also be prepared by slowly distilling its ammonium salt under pressure for about five hours at 220° to 230°.

$$RCOONH_4 \rightarrow RCONH_2 + H_2O$$

(3) Finally, they may be obtained from acid nitriles, which take up the elements of water when treated with moderately concentrated sulphuric acid ; *e.g.*,

$$\underset{\text{Acetonitrile}}{CH_3CN} + H_2O \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

---

[1] The reaction of an ester with ammonia is slow, and, in some cases the mixture may have to stand for several days.

13. Properties of Amides.—With the exception of formamide, which is a liquid, acid amides are colourless crystalline compounds. The lower members are readily soluble in water and, when pure, are colourless.

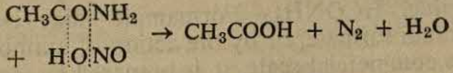
Reactions. The reactions of amides are as follows :—

(1) The basic character of ammonia having been considerably diminished by the introduction of an acyl group, amides are *neutral* towards litmus. However, they are **amphoteric in character** and possess weakly basic and weakly acidic characters. Thus, when dry hydrogen chloride is passed through an ethereal solution of acetamide, the hydrochloride, CH_3CONH_2HCl, is formed. On the other hand, hot aqueous solutions of amides dissolve mercuric oxide, forming compounds of the type, $(CH_3CONH)_2Hg$.

(2) When heated with alkalis or aqueous mineral acids, amides are hydrolysed to give the component acid and ammonia :

$$CH_3CONH_2 + HOH \rightarrow CH_3COOH + NH_3$$

(3) With nitrous acid, the parent acid and free nitrogen are produced (compare primary amines) :



$$\begin{array}{l} CH_3CO\vdots NH_2 \\ +\ \ H\,O\vdots NO \end{array} \rightarrow CH_3COOH + N_2 + H_2O$$

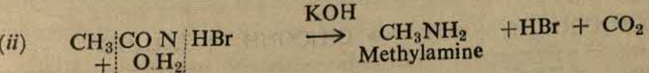
(4) When distilled with phosphorus pentoxide, they yield acid nitriles :

$$CH_3CONH_2 \rightarrow CH_3CN + H_2O$$

The dehydration can also be effected catalytically (page 126, reaction 3).

(5) **Hofmann's Bromamide Reaction.** When an amide is treated with bromine and aqueous potash, it forms an **amine containing one carbon atom less** than the amide ; *e.g.*,

$$(i)\quad \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{\text{Acetobromamide}}{CH_3CONHBr}$$



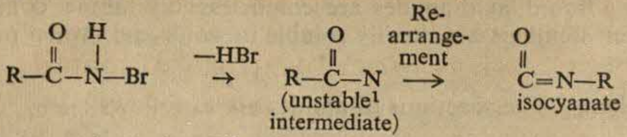
$$(ii)\quad \begin{array}{l} CH_3\vdots CO\,N\vdots HBr \\ \quad\ +\vdots\ O\,H_2\vdots \end{array} \xrightarrow{KOH} \underset{\text{Methylamine}}{CH_3NH_2} + HBr + CO_2$$

The reaction is carried out in **two steps** :

Step. I. The amide (1 mol) is cautiously mixed with bromine (1 mol) and a 10 per cent solution of potassium hydroxide (1 mol) is added, until the colour of bromine has been discharged.

Step. II. The reaction product from step I, containing acetobromamide, is added slowly to an excess of a cold concentrated solution of potassium hydroxide (3 mols).

The bromamide-to-amine reaction [equation (*ii*)] has been shown to actually occur through isocyanate formation,



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}Br} \xrightarrow{-\mathrm{HBr}} \underset{\text{(unstable}^{1}\text{ intermediate)}}{\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}N}} \xrightarrow{\text{Re-arrangement}} \underset{\text{isocyanate}}{\mathrm{\overset{\overset{O}{\|}}{C}{=}N{-}R}}$$

which then gets hydrolysed by the excess of alkali present to form an amine,

$$RNCO + 2KOH \rightarrow RNH_2 + K_2CO_3.$$

The reaction may be utilized for **descending a homologous series,** *i.e.*, for preparing a lower homologue from a higher one. Its most important application, however, is for the **preparation of primary amines.**

(6) *Reaction with Grignard Reagents.* The interaction of an amide with a Grignard reagent results in the production of a ketone (p. 219).

14. Constitution.—The constitution of amides is readily inferred from their formation from ammonia by the action of acid chlorides. The view is fully supported by the various reactions that these compounds undergo.

15. Formamide, $HCONH_2$.—Formamide may be prepared by heating ammonium formate, or by the action of ammonia on formic esters. On the commercial scale, it is prepared by catalytic combination of ammonia and carbon monoxide under high pressure.

Uses. Formamide is used in industry as a solvent, a hygroscopic agent and as a plasticizer.

16. Acetamide, CH_3CONH_2.—Acetamide is most readily obtained from ammonium acetate :

$$CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$$

Ammonium acetate crystals are boiled for 5 to 6 hours with an equal weight of glacial acetic acid under a reflux condenser, the acetic acid acting as a catalyst in the reaction. The product is subjected to fractional distillation (using an air condenser) in order to separate acetamide (b.p. 222°).

Another very convenient method is by the action of ammonia on ethyl acetate.

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

---

[1] The removal of HBr by the bromoamide leaves the nitrogen atom electronically deficient (with only six electrons in the valency shell). This deficiency induces migration of the alkyl group (together with the pair of shared electrons) from carbon to nitrogen as shown below :

The rearrangement thus creates a stable molecule with the nitrogen atom having a complete set of eight electrons in its valency shell.

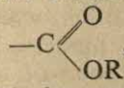
Acetamide crystallizes in colourless needles, m.p. 82° and b.p. 222°. It is readily soluble in water and alcohol. Its reactions have already been discussed (p. 329).

IV. ESTERS WITH MONOHYDRIC ALCOHOLS

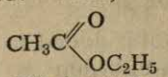
17. General.—A large number of esters occur in plants, especially in fruits and flowers, which owe their flavour and taste largely to these compounds. In their methods of formation and properties, the esters of monocarboxylic acids are similar to those of the mineral acids (p. 252).

Nomenclature of Esters.—

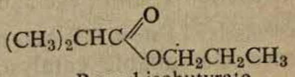
The chracteristic structural grouping present in carboxylic esters is



$—C(=O)OR$, where R is an alkyl or aryl group. The name of a particular ester is derived from (*i*) the name of the group, R, attached to oxygen and (*ii*) the name of the carboxylic acid from which the ester is derived. Thus, we have



Ethyl acetate



n-Propyl isobutyrate

18. Methods of Preparation of Esters :—

(1) **Direct Esterification.** The most commonly used method of preparing an ester is by the direct action of the acid on the alcohol. The reaction is *reversible*, *acid-catalysed* and involves the removal of a molecule of water between the *hydroxyl of the acid* and the hydrogen of the alcohol molecule (p. 231) :—

$$CH_3CO\underline{OH + H}OC_2H_5 \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

Since the reaction is reversible, various means are adopted to create optimum conditions for the production of the ester :—

(*i*) *Use of a Dehydrating Agent.* The hydrolytic action of the water produced may be minimized by the use of a dehydrating agent (concentrated H_2SO_4 or dry HCl gas).

(*ii*) **Fischer-Speier Method.** This is the simplest and the most frequently used method of esterification. It consists in refluxing the acid with an *excess of the alcohol* to which 3 to 5 per cent of HCl, or concentrated H_2SO_4, has been added to act as the catalyst[1]. The excess of the alcohol (which is generally cheaper than the acid) is employed to help the forward reaction as far forward as possible (Law of Mass Action). Conversely, if the alcohol is comparatively rare or more expensive, *excess of the acid* is used to bring about maximum esterification. After the equilibrium has been established

---

[1] In the case of esters of comparatively strong carboxylic acids (*e.g.*, formic and oxalic), no mineral acid need be added as catalyst.

(which may take several hours), the reaction product is poured into water, which dissolves the unchanged alcohol and the acid, while the ester separates out as an insoluble oil.

(*iii*) *Distilling out Water.* In the case of high boiling reactants, esterification can be brought about very simply by distilling out the water as it is formed.

(*iv*) *Distilling out Ester.* In the case of a low boiling ester (*e.g.*, methyl formate, b.p. 32°, and ethyl formate, b.p. 54°) a mixture of the alcohol and the acid is refluxed and the ester produced is allowed to distil out as rapidly as formed.

The rate of esterification is very much dependent on the structure of the alcohol and of the acid. Primary alcohols possess the maximum reactivity and the tertiary alcohols the minimum. In other words, branching on the hydroxyl-carrying carbon atom hinders the reaction. Similarly, the branching on the *alpha*-carbon of the carboxylic acid retards esterification.

(2) **Esterification of Alcohols with Acid Chlorides or Anhydrides.** *See* page 323, reaction 2, and page 326, reaction 2.

(3) **Alcoholysis of Esters.** When an alcohol is added to an ester in the presence of a suitable catalyst, an equilibrium is gradually set up :—

$$CH_3COOR + R'OH \rightleftharpoons CH_3COOR' + ROH,$$

which may be shifted towards the right : (*i*) by the use of a *large excess* of the alcohol R'OH or (*ii*) by the removal of the alcohol ROH. The usual practice is to treat an ester with a large excess (about 10 times) of the necessary alcohol containing a little sodium alkoxide in solution. The method has proved particularly useful in the preparation of esters of acids present in fats and oils. Thus, Reid and others have been able to prepare *n*-butyl oleate from olive oil in a 70 per cent yield.

(4) **From Aldehydes.** Esters, in good yield, can be obtained from aldehydes by the Tischenko reaction (p. 279).

(5) **From Salts of Carboxylic Acids.** A method of fairly general application consists in treating metallic salts of carboxylic acids with alkylating agents (alkyl halides or dialkyl sulphates) *e.g.*,

(*i*) $CH_3COOAg + C_2H_5I \rightarrow CH_3COOC_2H_5 + AgI$

(*ii*) $RCOOK + (CH_3)_2SO_4 \rightarrow RCOOCH_3 + CH_3KSO_4$

(6) **Special Methods.** In certain cases, special methods have proved very useful for the preparation of esters. We may here mention the following :—

(*i*) *Methyl esters* of carboxylic acids can be prepared in high yields by the action of *diazomethane* (ethereal solution of the gas) on the acids. The reaction occurs at room temperature with evolution of nitrogen :—

$$CH_3COOH + \underset{\text{Diazomethane}}{CH_2N_2} \rightarrow CH_3COOH_3 + N_2$$

The method is particularly important for the preparation of methyl esters of rare or expensive acids. As diazomethane is *highly poisonous and explosive*, utmost care must be taken in its preparation and use.

(*ii*) *Esters of formic acid* have been prepared in good yields by the interaction of *carbon monoxide* and liquid alcohols at high pressure in the presence of a catalyst (*e.g.*, sodium)

$$C_2H_5OH + CO \rightarrow \underset{\text{Ethyl formate}}{HCOOC_2H_5}$$

(*iii*) *Esters of acetic acid* can be easily prepared by the action of *ketene* (*see* footnote 2, page 327) on alcohols ; *e.g.*,

$$CH_2{=}CO + C_2H_5OH \rightarrow CH_3COOC_2H_5$$

19. Physical Properties of Esters.—The lower members are colourless liquids possessing an agreeable, fruity odour. They are generally insoluble in water, but soluble in alcohol and ether.

In Fig. 3, the boiling points of esters of the normal fatty acids are plotted against the number of carbon atoms in the component alcohols.

20. Reactions of Esters.—Esters are very reactive substances, and in most of their reactions the alkoxyl group,—OR, is replaced by other groups. The chief reactions of esters are:

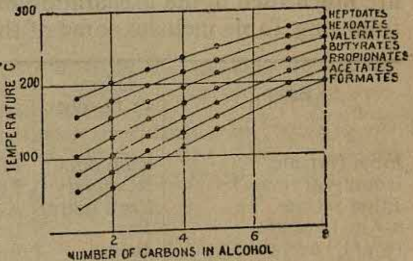


Fig. 3. Boiling points of Esters.

(1) *Hydrolysis.* Hydrolysis or the replacement of —OR by —OH, which is the reversal of esterification, may be effected by heating an ester with water under pressure :

$$CH_3COOC_2H_5 + HOH \rightleftharpoons CH_3COOH + C_2H_5OH$$

A large amount of water is necessary to displace the equilibrium towards the right. The reaction is catalysed by the addition of a small quantity of a mineral acid.

The hydrolysis of an ester can be carried out *quantitatively* in the presence of an alkali. The latter serves two purposes: (*i*) it acts catalytically, and (*ii*) it combines with the acid produced, thus making the reaction proceed to completion :

$$\begin{array}{l} CH_3COOC_2H_5 + HOH \rightleftharpoons CH_3COOH + C_2H_5OH \\ \underline{\quad CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \quad} \\ CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH \end{array}$$

Hydrolysis of an ester by means of an alkali is termed *saponification*, since the making of soap is a useful application of this reaction.

(2) *Alcoholysis. See* p. 332, method 3.

(3) *Ammonolysis.* The replacement of the —OR group of an ester by the —NH_2 group by means of ammonia is employed for the preparation of amides (page 328, reaction 1).

(4) *Reaction with Grignard Reagents* (*See* page 218, reaction 3(*i*)).

(5) *Reduction to Alcohols* (*See* page 228).

21. Identification of an Ester.—An ester can be identified by boiling it under a reflux condenser with an excess of 10 per cent sodium hydroxide solution until no more oily drops of the ester are visible :

$$RCOOR' + NaOH \rightarrow RCOONa + R'OH.$$

The product is then distilled, until about one-third has passed over. The distillate is examined for the alcohol and the residual liquid in the flask for the acid component. If the alcohol be non-volatile, it is extracted with ether.

22. Uses of Esters.—Esters are put to the following important uses :—

(1) On account of their pleasant fruity or flowery odours, esters are much used in the preparation of **synthetic flavours and perfumes.** The following Table includes some of the esters used in this direction :—

Ester	Odour or flavour	Ester	Odour or flavour
Ethyl formate	Rum odour	Methyl butyrate	Pineapple
Isobutyl formate	Raspberry	Ethyl ,,	,,
Ethyl acetate	Fruit odour	Armyl ,,	Apricot
n-Amyl acetate	Pear	Isoamyl valerate	Apple
Isoamyl acetate	Banana	Ethyl nonylate	Rose
Octyl acetate	Orange	Ethyl undecylenate	Violet
Benzyl butyrate	Jasmine	Methyl salicylate	Wintergreen

(2) Very large quantities of esters are now employed as solvents for nitro-cellulose and other materials used in the preparation of lacquers and films. They are not only good solvents but also possess the valuable property of evaporating rapidly. Ethyl acetate, butyl acetate, amyl acetate and butyl oleate are the more important examples of esters used in the manufacture of lacquers and films.

(3) Some esters find important application in organic synthesis. Ethyl orthoformate, ethyl malonate and ethyl acetoacetate are important examples.

(4) Waxes, fats and oils are also of the nature of esters, and find special uses.

23. Ethyl Acetate, $CH_3COOC_2H_5$.—This ester is prepared in the laboratory by the interaction of ethyl alcohol and acetic acid in the presence of concentrated sulphuric acid, which serves to remove the water formed in the reaction.

Expt. 3. A mixture of 50 ml. each of alcohol and concentrated sulphuric acid is placed in a distillation flask attached to a condenser and fitted with a dropping funnel and a thermometer, the bulb of the latter dipping completely into the liquid (Fig. 4). The flask is heated on a sand bath until the temperature has risen to

140°C when a mixture of 100 ml. each of alcohol and glacial acetic acid is run in from the dropping funnel at the rate at which the liquid distils. The temperature must be kept as near 140°C as possible throughout the experiment.

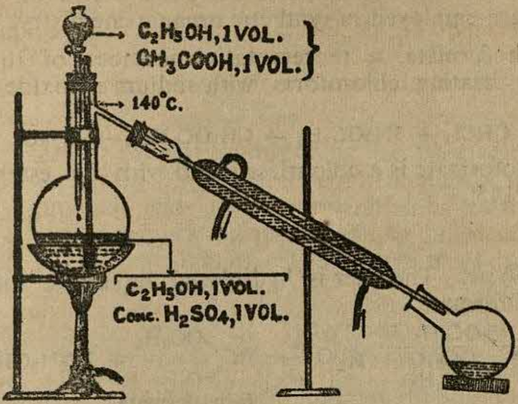


Fig. 4. Preparation of Ethyl Acetate.

The distillate contains alcohol, acetic acid, water and sulphur dioxide in addition to ethyl acetate. It is purified by shaking in a separating funnel, first with sodium carbonate solution, until neutral, and then with a saturated solution of common salt, to remove alcohol. The upper layer, consisting of the ester, is separated and dried by allowing it to stand overnight in contact with granulated calcium chloride. It is then filtered into a dry distillation flask and distilled, the fraction boiling at 75° to 79° being collected separately.

Commercial Preparation :—

(1) *Distillation process.* Most of the ethyl acetate of commerce is now manufactured by the interaction of the alcohol and the acid in a fractionating column. Acetic acid containing proper amount of catalyst is fed into the column, where it comes in contact with ethyl alcohol. The esterification takes place in the fractionating column itself and the **minimum-boiling ternary mixture** of ethyl acetate, ethyl alcohol and water containing 83·2 per cent of the ester is taken from the top of the column.

(2) *Vapour Phase Esterification.* In this method, the acid and the alcohol, in the vaporous state, are passed over silica gel catalyst at 150°, when an equilibrium mixture containing 85 per cent of the ester is obtained.

(3) *From Acetaldehyde.* A third method for the manufacture of ethyl acetate is from acetaldehyde through the Tischenko reaction page 279).

Properties. Ethyl acetate boils at 77°, and is soluble in 17 parts of water. It has a specific gravity of 0·9.

Uses. On account of its refreshing perfume, ethyl acetate is employed in the preparation of artificial fruit essences and in medicine. It is also used as a solvent in the manufacture of smokeless powder.

24. Ethyl orthoformate, $HC(OC_2H_5)_3$.—Orthocarboxylic acids, $R.C(OH)_2$, do not exist in the free state, but their esters are well known. Of these the most important are the esters of orthoformic acid, which are employed in synthetic organic chemistry.

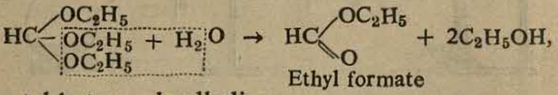
Ethyl orthoformate, a representative member of this class, is obtained by heating chloroform with sodium ethoxide in alcoholic solution,

$$CHCl_3 + 3NaOC_2H_5 \rightarrow CH(OC_2H_5)_3 + 3NaCl$$

Ethyl orthoformate is a colourless liquid with an ester-like smell, and boils at 145°.

Reactions :—

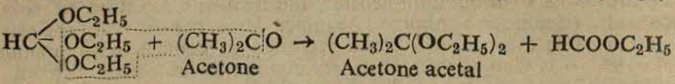
(1) *Hydrolysis.* The ester is hydrolysed by dilute mineral acids to give ethyl formate,



$$HC\begin{cases}OC_2H_5\\OC_2H_5 + H_2O\\OC_2H_5\end{cases} \rightarrow \underset{\text{Ethyl formate}}{HC\begin{cases}OC_2H_5\\O\end{cases}} + 2C_2H_5OH,$$

but is very stable towards alkalis.

(2) *Reaction with Aldehydes and Ketones.* This reaction is used in the preparation of acetals of aldehydes and ketones ; *e.g.*,



$$HC\begin{cases}OC_2H_5\\OC_2H_5 + \underset{\text{Acetone}}{(CH_3)_2CO}\\OC_2H_5\end{cases} \rightarrow \underset{\text{Acetone acetal}}{(CH_3)_2C(OC_2H_5)_2} + HCOOC_2H_5$$

(3) *Reaction with Grignard Reagents.* This reaction yields an aldehyde as the final product [see p. 217, reaction (*iii*)].

QUESTIONS

1. Describe the preparation of a *pure* specimen of acetyl chloride. To what use is it put in the laboratory ?

2. Indicate briefly the methods for the manufacture of acetic anhydride. (*Lucknow, B.Sc., Prev., 1952*)

3. Describe the methods employed for the detection and estimation of the hydroxyl group. (*Punjab, B.Sc., 1936*)

4. Give the general methods for the preparation of amides and their chief chemical properties. To what use can amide-formation be put in synthetic chemistry ?

5. Describe the preparation of acetamide. How may acetic acid, acetonitrile and methylamine be obtained from it ?

6. A substance gave the following results on analysis :—0·197 gm. gave 0·293 gm. CO_2 and 0·150 gm. H_2O. By the Kejeldahl method 0·59 gm. required 10 ml. of normal H_2SO_4 for neutralization of the ammonia. The original substances when boiled with caustic soda evolved ammonia, and the dry residue, when heated with soda-lime gave off methane. Whot was the substance ? Explain the above reactions.
Ans. Acetamide. (*Punjab, B.Sc. Hons., 1924*)

7. A substance on analysis gave C=40·57, H=8·53 and N=23·65 per cent. This substance was treated with bromine and caustic potash solution ; the product was found to yield a salt with hydrochloric acid and to evolve nitrogen with nitrous acid. Assign a formula to the substance.
Ans. Acetamide, CH_3CONH_2 (*Punjab, B.Sc., 1930*)

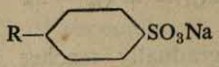
become available in recent years. Three groups of such detergents are now in use :

(1) **Sodium Alkyl Sulphates.** Sodium salts of alkyl-sulphuric acids having 10 or more carbon atoms in the alkyl group, *e.g.*,

$C_{12}H_{25}SO_4Na$	$C_{16}H_{33}SO_4Na$	$C_{18}H_{37}SO_4Na$
Sodium laurylsulphate	Sodium cetylsulphate	Sodium stearylsulphate

possess good detergent properties, and may be used with sea water and hard waters, as the calcium and magnesium alkylsulphates are soluble. Alkylsulphuric acids are prepared either by esterification of synthetically prepared higher alcohols or by the addition of sulphuric acid to higher alkanes. The detergents of this class are extensively used in the textile industry.

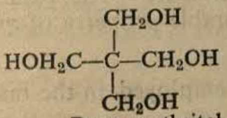
Another important source of detergents of this class is petroleum. The high boiling fractions are submitted to chlorination and the alkyl chlorides thus obtained are treated with benzene in the presence of anhydrous aluminium chloride (Friedel and Crafts' reaction). The resulting alkylbenzenes containing a long-chain alkyl group, R, is submitted to sulphonation, followed by the neutralization of the product with sodium carbonate. The sodium salts,



thus obtained are good detergents.

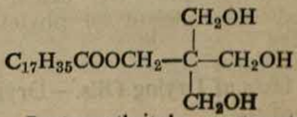
(2) **Cation-Active Soaps** (or *Invert Soaps*). In these, as the name implies, the active part of the molecule is the cation. They are quarternary ammonium salts containing one or more long-chain alkyl groups. A representative of this class is **trimethyl stearyl-ammonium bromide,** $\left(\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}N{<}\genfrac{}{}{0pt}{}{CH_3}{C_{18}H_{37}}\right)Br$. Some of the members of this class possess remarkable bactericidal properties.

(3) **Partially Esterified Polyhydroxy Compounds.**—This group is obtained from polyhydroxy compounds by partial esterification with a higher fatty acid. A typical example is the monostearate of penta-erythritol :—



$$\begin{array}{c} CH_2OH \\ | \\ HOH_2C{-}C{-}CH_2OH \\ | \\ CH_2OH \end{array}$$

Penta-erythritol
(Tetrahydroxymethyl-methane)



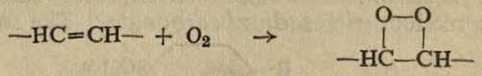
$$\begin{array}{c} CH_2OH \\ | \\ C_{17}H_{35}COOCH_2{-}C{-}CH_2OH \\ | \\ CH_2OH \end{array}$$

Penta-erythritol monostearate

18. Action of Detergents.—Detergents act by lowering the surface tension of water. Their aqueous solutions will, therefore, more readily wet the particles of dirt to be removed than water itself. The molecule of a detergent contains one group which confers water-solubility (*hydrophilic group*) and one which has the opposite effect (*hydrophobic group*). Thus, in common soap carboxyl group is hydrophilic and the long-chain alkyl group is hydrophobic. When a detergent is used in washing, it emulsifies oil, grease and dirt by surrounding the individual particles of those in such a manner that the hydrophilic end of the detergent molecule is in the water, while the hydrophobic end is towards the emulsified particle.

19. Drying Oils.—Certain fatty oils (notably linseed, perilla, tung and oiticica oils), when exposed to air in thin layers, absorb oxygen (upto 30 per cent by weight) to form tough, elastic, water-insoluble films. For this reason, such oils are called "**drying oils**". The drying character of these oils is due to the presence of glycerides of certain acids containing two or three double bonds, namely linoleic, linolenic, eleostearic and licanic acids (*see* list on page 358). Oils containing glycerides of acids having *conjugated* double bonds (tung and oiticica, which contain high percentage of eleostearic and licanic acids, dry very much more readily than those containing glycerides of acids with non-conjugated double bonds (linseed and perilla, which contain linoleic and linolenic acids).

During the first stage of drying, oxygen is added at the double bonds to form peroxides :—



$$-HC{=}CH- + O_2 \rightarrow \begin{array}{c} O-O \\ |\quad\;\; | \\ -HC-CH- \end{array}$$

The peroxide content gradually reaches a maximum and then disappears owing to polymerization, which finally results in the production of a tough **linoxylin film.** The peroxides, first produced, play the role only of a catalyst during the polymerization process, which ultimately results in the production of a **three-dimensional system** constituting the linoxylin film.

Though tung and oiticica oils are very much superior to linseed oil, their use is restricted on account of cost. The most widely used drying oil is linseed oil. The **raw linseed oil**, however, absorbs oxygen so slowly that paints made from it would be useless from the practical point of view. The difficulty is met by heating the oil to 200° with the addition of certain substances, called **driers**. These, in modern practice, consist of oil-soluble cobalt, manganese and lead salts of long-chain fatty acids, such as linolenic. The resulting so-called **boiled linseed oil** possesses the desirable property of quick drying.

20. Uses of Drying Oils.—Drying oils are employed in the manufacture of :—

(1) *Paints.* These are prepared by grinding a pigment (white lead, red lead, chrome yellow, *etc.*) with linseed oil containing a drier. When an especially quick-drying paint is required, turpentine or light petroleum is added to the drying oil. This makes the paint thin and permits a more even coating. The turpentine evaporates away quickly, leaving a thin coating of the paint behind, which dries by absorbing oxygen in the usual manner.

(2) *Oil Varnishes.* These are made by adding a drying oil to a solution of a natural resin in a volatile organic solvent. The solvent evaporates and the oil dries by absorption of oxygen. The result is a protective, glossy film, the gloss being due to the presence of resin.

(3) *Printing Ink.* This is made by grinding together carbon black, a drying oil and a drier.

(4) *Oil Cloth.* This is prepared by applying two or three coatings of linseed oil paint on canvas.

(5) *Linoleum.* This is made by cementing ground cork with thickened linseed oil and resin, and pressing it on a fabric backing.

21. Other Uses of Fats and Oils.—In addition to the chief uses of fats and oils described in the foregoing pages, there are numerous minor uses, a few of which are given below :—

(1) *In Pharmacy.* Thus, cold-pressed castor oil and croton oil are used as purgatives. Almond oil is used both internally and externally. Cod-liver oil is prescribed in wasting diseases.

(2) *As Lubricants.* Lower grades of castor oil, certain fish oils, and many others are used as lubricants.

(3) *As Hair Oils.* Refined vegetable oils of non-drying character are used as hair oils.

(4) *As Illuminants.* Sarson oil is sometimes used as an illuminant in villages. Other vegetable oils and fish oils are used similarly.

QUESTIONS

1. Write a brief note on the chemical composition of oils and fats, and explain the significance of *saponification value* and *iodine value* as applied to fatty oils. (*Osmania, B.Sc., 1953*)

2. What do you understand by the term 'Glyceride'? Give examples of various types of simple glycerides and mixed glycerides. Discuss the importance of glycerides in industry. (*Andhra, B.Sc., 1952*)

3. What are soaps? Describe how you would prepare a sample of soap by the cold process. How is glycerin recovered as a by-product in the manufacture of boiled soaps? (*Madras, B.A., 1942*)

4. Describe in detail the Hot Process for the manufacture of soap. Draw a conventional diagram of the complete plant used in a modern soap factory.

5. What are *drying oils*? To what main use are they put in industries? Explain the process for drying of such oils.

6. How would you distinguish between two substances having the formula C_3H_6O?

Define the terms wax, fat and oil. Give the names and structures of the important acids formed on hydrolysis of (*a*) carnauba wax, (*b*) coconut oil (*c*) linseed oil and olive oil. (*Lucknow, B.Sc., 1962*)

7. Write an account of the industrial uses of oils and fats. (*Poona, B.Sc., 1956*)

8. What are oils and fats? Define the various oil constants and state their significance in evaluating the quality of an oil. What changes take place during the hardening of an oil and how is it brought *about*? (*Panjab, B.Sc., 1956*)

9. What is the chemical character of a fat? Explain the difference between oils, fats and waxes. Distinguish between mineral, vegetable and essential oils. (*Gorakhpur, B.Sc., 1961*)

10. Define and give examples of:

(*a*) Saponification value (*b*) Iodine value (*c*) Hardening of oils. (*Lucknow, B.Sc., 1956*)

11. Write an essay on the industrial uses of fats and oils. (*Lucknow, B.Sc., 1959*)

12. Write an essay on Fats and Oils. (*Lucknow, B.Sc., 1962*)

13. What are fats and oils? What products are formed when they are saponified? How can a vegetable oil be distinguished from a mineral oil? (*Calcutta, B.Sc., 1957, 1959*)

14. Define 'Iodine Value'.

What are oils, fats and waxes? How has the constitution of these substances been determined? (*Gauhati, B.Sc., 1954*)

15. To what class of organic compounds do fats and oils belong? How would you prove your statement? Describe how you would proceed to obtain three organic substances from a particular fat or oil which you will choose for your experiment. (*Calcutta, First M.B.B.S., 1959*)

16. What are neutral fats? Write what you know about their chemistry.

How has fat been obtained from oils? How can you differentiate a vegetable oil from a mineral oil? (*Calcutta, B.Sc., 1947*)

17. What is the chemical nature of a fat? How does it differ from an oil? Give briefly the manufacture of soap. (*Banaras, B.Sc., 1953*)

81. Give a brief account of the Chemistry of fats and oils, the methods of their analysis and their industrial uses. (*Kerala, B.Sc., 1957*)

19. What is the chemical nature of a fat? How would you distinguish between animal fat and vegetable one? What are the commercial uses of oils and fats? (*Agra, B.Sc., 1958*)

20. What are Iodine value and Saponification value? Discuss the principles underlying the manufacture of soap. (*Jammu & Kashmir, B.Sc., 1960*)

21. What is the chemical nature of oils and fats. Explain the significance of :—

(*a*) Acid value; (*b*) Saponification value; and (*c*) Iodine value. (*Venkateswara, B.Sc., 1962*)

22. Write an essay on the chemistry and industrial uses of Fats and Oils. (*Gorakhpur, B.Sc., 1962*)

CHAPTER TWENTY-THREE

DICARBOXYLIC ACIDS

1. Nomenclature.—Dicarboxylic acids contain *two* carboxyl groups in the molecule. Besides common names, which are very frequently used for lower dibasic acids, there exist two different systems of nomenclature.

(1) In the **I.U.C. system**, dicarboxylic acids are regarded as the **oxidation products of hydrocarbons**, and are named after them by adding the suffix **-diacid** or **-dioic acid** to the name of the parent hydrocarbon. The following are some illustrative examples :—

HOOC.COOH	$HOOC(CH_2)_2COOH$	HOOCCH = CHCOOH
Ethanedioic acid	Butanedioic acid	Butenedioic acid
or Ethane diacid	or Butane diacid	or Butene diacid

(2) In the other system, which is of more frequent use in literature of organic chemistry, dibasic acids are regarded as **dicarboxylic substitution products of hydrocarbons**, and are named accordingly. The following few will serve as illustrative examples :—

$HOOC.CH_2.COOH$	$HOOC(CH_2)_2COOH$
Methanedicarboxylic acid	1,2-Ethanedicarboxylic acid
$\overset{4}{C}H_3\overset{3}{C}H(COOH)\overset{2}{C}H_2\overset{1}{C}H_2COOH$	$HOOCCH_2CH_2CH_2CH_2COOH$
1,3-Butanedicarboxylic acid	1,4-Butanedicarboxylic acid

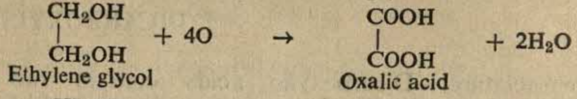
1. SATURATED DIBASIC ACIDS

2. General.—The most important series of saturated dibasic acids is the **alpha-omega series**, *i.e.*, the one in which the two carboxyls are at the two ends of a *straight* chain of carbon atoms. The general formula of the series is $HOOC(CH_2)_nCOOH$. The following table gives the common name, formula, melting point, solubility in water and the dissociation constant for the first stage of ionization in the case of the first nine members of the series.

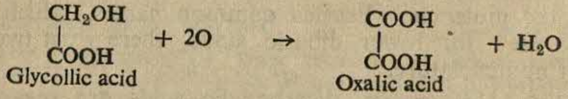
Name of the acid	Formula	M. P. °C	Solubility in gm/100 gm H_2O	Primary ionization constant
Oxalic	HOOC.COOH	188	8·6 at 20°	0·1
Malonic	$HOOCCH_2COOH$	133	73·5 ,,	0·00163
Succinic	$HOOC(CH_2)_2COOH$	185	6·8 ,,	0·000065
Glutaric	$HOOC(CH_2)_3COOH$	98	63·9 ,,	0·000047
Adipic	$HOOC(CH_2)_4COOH$	153	1·5 ,,	0·000038
Pimelic	$HOOC(CH_2)_5COOH$	105	5·0 ,,	0·000032
Suberic	$HOOC(CH_2)_6COOH$	142	0·16 ,,	0·000030
Azelaic	$HOOC(CH_2)_7COOH$	106	0·24 ,,	0·000029
Sebacic	$HOOC(CH_2)_8COOH$	134	0·10 ,,	0·000028

3. General Methods of Formation.—

(1) By the oxidation of di-primary glycols, hydroxy-acids containing a CH_2OH group, and of many complex compounds, such as fats, fatty acids, and carbohydrates ; *e.g.*,



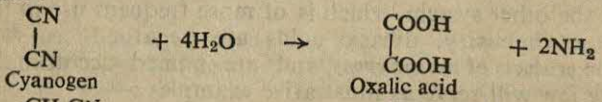
$$\underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + 4O \rightarrow \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 2H_2O$$



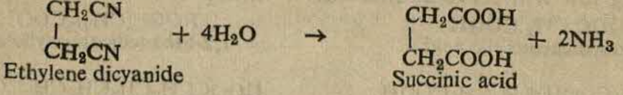
$$\underset{\text{Glycollic acid}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}} + 2O \rightarrow \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + H_2O$$

The formation of oxalic acid from cane-sugar or sawdust, of azelaic acid from oleic acid, and of adipic acid from fats are examples of the production of dibasic acids by the oxidative breakdown of complex organic compounds.

(2) By the hydrolysis of the corresponding di-nitriles and cyano-fatty acids :

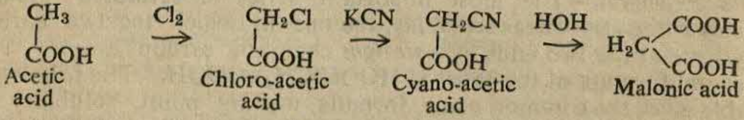


$$\underset{\text{Cyanogen}}{\begin{matrix}CN\\|\\CN\end{matrix}} + 4H_2O \rightarrow \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 2NH_2$$



$$\underset{\text{Ethylene dicyanide}}{\begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix}} + 4H_2O \rightarrow \underset{\text{Succinic acid}}{\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}} + 2NH_3$$

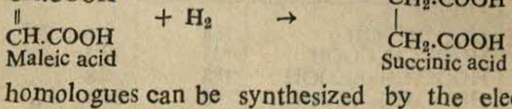
Indirectly, this reaction can be utilized for the preparation of a dibasic acid from a halogen substituted acid, hydroxy-acid, or a fatty acid. Thus :



$$\underset{\text{Acetic acid}}{\begin{matrix}CH_3\\|\\COOH\end{matrix}} \xrightarrow{Cl_2} \underset{\text{Chloro-acetic acid}}{\begin{matrix}CH_2Cl\\|\\COOH\end{matrix}} \xrightarrow{KCN} \underset{\text{Cyano-acetic acid}}{\begin{matrix}CH_2CN\\|\\COOH\end{matrix}} \xrightarrow{HOH} \underset{\text{Malonic acid}}{H_2C{<}\begin{matrix}COOH\\COOH\end{matrix}}$$

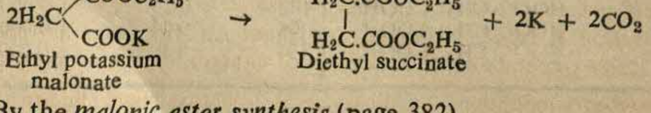
A hydroxy-acid (*e.g.*, glycollic acid, $CH_2OH.COOH$) may be converted, by treatment with PCl_5, into a chloro-substituted acid, and the latter is then transformed into a dibasic acid as above.

(3) Unsaturated dicarboxylic acids may be reduced to the corresponding saturated acid by hydrogenation :



$$\underset{\text{Maleic acid}}{\begin{matrix}CH.COOH\\\|\\CH.COOH\end{matrix}} + H_2 \rightarrow \underset{\text{Succinic acid}}{\begin{matrix}CH_2.COOH\\|\\CH_2.COOH\end{matrix}}$$

(4) Higher homologues can be synthesized by the electrolysis of ethyl-potassium salts of the simplest members. Thus :



$$\underset{\text{Ethyl potassium malonate}}{2H_2C{<}\begin{matrix}COOC_2H_5\\COOK\end{matrix}} \rightarrow \underset{\text{Diethyl succinate}}{\begin{matrix}H_2C.COOC_2H_5\\|\\H_2C.COOC_2H_5\end{matrix}} + 2K + 2CO_2$$

(5) By the *malonic ester synthesis* (page 382).

4. Physical Properties.—The acids of the oxalic series are well-defined crystalline substances.

The melting points and solubility relationships (*see* table, page 373) divide the acids into two types, one containing an even number of carbon atoms and the other an odd number. The former melt much higher than the latter. With the increasing number of carbon atoms, the melting points of the former group gradually fall, while those of the latter gradually rise. Thus, the melting points of the even and the odd series approximate more closely with rising molecular weight. This relationship is represented graphically in Fig. 1.

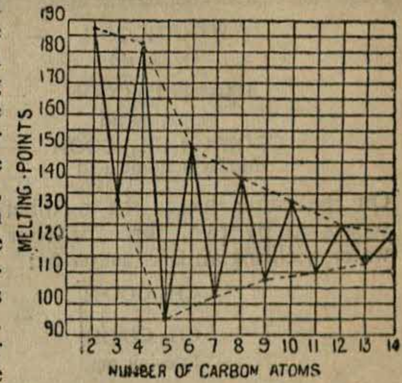


Fig. 1. Melting points of saturated dibasic acids.

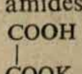
In the case of the lower members, the solubility of the acids having an even number of carbon atoms is considerably lower than of those with an odd number of carbon atoms. In both the series, the solubility falls with the increasing molecular weight, but while the fall in the case of the even series is gradual, that in the odd series is quite abrupt. Thus, here also the values come nearer together as the series is ascended.

Dicarboxylic acids ionize in two steps. Thus, for oxalic acid we have :—

$$\mathrm{HOOC.COOH} \rightleftharpoons \mathrm{HOOC.COO^-} + \mathrm{H^+}$$
$$\mathrm{HOOC.COO^-} \rightleftharpoons \mathrm{^-OOC.COO^-} + \mathrm{H^+}$$

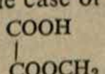
From the primary[1] ionization constants given in the Table on page 373, it may be seen that oxalic acid is one of the strongest of organic acids (compare formic acid). It is more than sixty times as strong as the next member, malonic acid. The following members are very much weaker as compared with the first two.

5. Chemical Properties.—(1) The dicarboxylic acids show the usual properties of the carboxyl group, and form *two* series of salts, esters and amides. Thus, in the case of oxalic acid we have :—



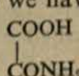
$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOK}\end{array}$$

Acid potassium oxalate



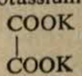
$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOCH_3}\end{array}$$

monomethyl oxalate



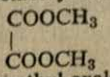
$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{CONH_2}\end{array}$$

Oxamic acid



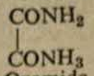
$$\begin{array}{c}\mathrm{COOK}\\ |\\ \mathrm{COOK}\end{array}$$

Normal potassium oxalate



$$\begin{array}{c}\mathrm{COOCH_3}\\ |\\ \mathrm{COOCH_3}\end{array}$$

Dimethyl oxalate



$$\begin{array}{c}\mathrm{CONH_2}\\ |\\ \mathrm{CONH_3}\end{array}$$

Oxamide

(2) *Action of Heat.* The action of heat on the various members of the series depends on the number of carbon atoms separating the

---

[1] The *primary* ionization of a dibasic acid is always much higher than the secondary.

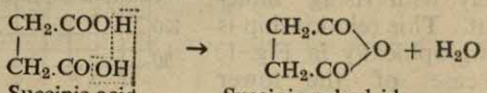
two carboxyl groups. When the two carboxyls are directly linked together, as is the case with oxalic acid, or when they are separated by not more than one carbon atom, as in malonic acid and alkylmalonic acids, decomposition occurs with **evolution of carbon dioxide and production of a monocarboxylic acid**; *e.g.*,

$$\underset{\text{Oxalic acid}}{H\,\vdots OOC\vdots .COOH} \longrightarrow \underset{\text{Formic acid}}{HCOOH} + CO_2$$

$$\underset{\text{Malonic acid}}{H\,\vdots OOC\vdots CH_2.COOH} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

$$\underset{\text{Methylmalonic acid}}{COOH.CH(CH_3).COOH} \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH} + CO_2$$

On the other hand, the members, in which the two carboxyls are separated by two, three or four carbon atoms, lose a molecule of water, yielding an **inner anhydride** :

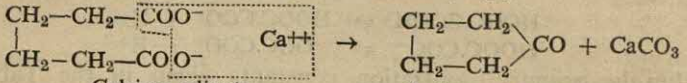


$$\begin{array}{l}CH_2.COO\,H\\ |\\ CH_2.CO\,OH\end{array} \rightarrow \left.\begin{array}{l}CH_2.CO\\ |\\ CH_2.CO\end{array}\right> O + H_2O$$

Succinic acid Succinic anhydride

The anhydride formation is particularly marked in those cases where, by elimination of water, a 5- or 6-membered ring is formed. Acid in which the two carboxyls are separated by more than 4 carbons, when heated, either volatilize as such, or undergo profound decomposition, accompanied by charring.

(3) *Action of Heat on Calcium Salts.* The calcium salts of dicarboxylic acids, in which the anhydride-formation takes place readily, decompose on heating, yielding **cyclo-ketones** ; *e.g.*,



$$\begin{array}{l}CH_2-CH_2-COO^-\\ |\\ CH_2-CH_2-COO^-\end{array} Ca^{++} \rightarrow \left.\begin{array}{l}CH_2-CH_2\\ |\\ CH_2-CH_2\end{array}\right> CO + CaCO_3$$

Calcium adipate Cyclo-pentanone

6. Oxalic Acid, *Ethanedioic Acid*, HOOC.COOH.—This acid occurs very extensively in the vegetable kingdom, particularly in plants of the *oxalis* and *rumex* families, in the form of potassium hydrogen oxalate or calcium oxalate. Sometimes, it occurs in plant cells as a crystalline deposit of the calcium salt.

Synthesis. Oxalic acid may be synthesized by the general reactions described in sec. 3.

Laboratory Preparation. Oxalic acid can be most readily obtained in the laboratory by the oxidation of cane-sugar with nitric acid. The oxidation proceeds very vigorously, and abundant nitrous fumes are evolved :

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O$$
$$C_{12}H_{22}O_{11} + 18O \rightarrow 6H_2C_2O_4 + 5H_2O$$

Expt. 1. *Preparation of Oxalic acid* :—

Cane-sugar, 50 gm.

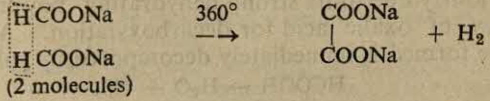
Concentrated nitric acid, 150 ml.

The nitric acid is placed in a large flask, and the sugar is added. The flask is heated on a water-bath in a fume-closet, until the reaction begins, after which it is allowed to proceed without the application of heat. When the reaction has moderated, the liquid is transferred to a dish and concentrated to a small bulk by evaporation on a water bath. On being allowed to cool, the concentrated solution deposits colourless crystals of oxalic acid, $(COOH)_2.2H_2O$. The acid is obtained pure by recrystallization from hot water.

Commercial Preparation. The modern method for the large-scale preparation of oxalic acid is **from carbon monoxide *via* sodium formate.** The first step in the process is the production of sodium formate by heating anhydrous sodium hydroxide with carbon monoxide under high pressure :

$$NaOH + CO \rightarrow HCOONa$$

The resulting sodium formate is heated at 360° (in the presence of sodium hydroxide or carbonate), when sodium oxalate is produced with the evolution of hydrogen :



$$\begin{matrix} H\,COONa \\ H\,COONa \\ \text{(2 molecules)} \end{matrix} \xrightarrow{360^\circ} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

The sodium oxalate is dissolved in water, and boiled with milk of lime, when calcium oxalate is precipitated. This is filtered off, suspended in water and agitated with dilute sulphuric acid, when calcium sulphate precipitates out. The precipitate is removed by filtration, and the solution evaporated to obtain crystals of oxalic acid.

Formerly, oxalic acid was prepared on the commercial scale by heating saw-dust with alkali at 240° to 250°, when sodium oxalate was produced (the oxalic acid being derived from cellulose, which contains the unit—CHOH.CHOH—). Free acid was obtained from the alkali oxalate as described above.

Properties. Oxalic acid crystallizes with $2H_2O$, and possesses two melting points. The hydrated acid melts at 101°, and the anhydrous form, at 190°. It is fairly soluble in water, the saturated solution at the ordinary temperature being about 2N.

Like other dicarboxylic acids, oxalic acid forms *two* series of salts, esters and amides. With phosphorus pentachloride, both the carboxyl groups are simultaneously attacked, and *oxalyl chloride*, ClCO.COCl, is produced. For this reason, the half-chloride, HOOC.COCl, is not known.

Special Properties of Oxalic Acid.—

The two carboxyl groups in the oxalic acid molecule are *directly* linked together and not through a hydrocarbon residue, as is the case with other members of the series. This peculiarity of structure confers the following special properties on the oxalic acid molecule :—

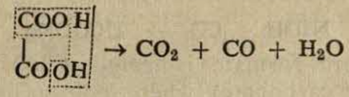
(1) *Exceptionally Strong Acidic Character.* As already stated, oxalic acid is one of the strongest of organic acids, being about 3000 times as strong as most of the other members of the series (see Table on p. 373). This is due to the strong **inductive influence** of one carboxyl group on the other, which promotes ionization of the latter.

Because of oxalic acid being an unusually strong organic acid, it is often employed as a condensing agent in reactions where mineral acids cannot be used on account of their destructive action.

(2) *Decarboxylation.* Oxalic acid has great tendency to lose carbon dioxide (decarboxylation). Thus, when carefully heated above its melting point, it yields formic acid :—

$$\mathrm{H\boxed{OOC}COOH \rightarrow HCOOH + CO_2}$$

Rapid heating results in decarboxylation of both the carboxyls as follows :



$$\left.\begin{array}{l}\mathrm{COO\,H}\\ |\\ \mathrm{CO\,OH}\end{array}\right| \rightarrow \mathrm{CO_2 + CO + H_2O}$$

Sulphuric acid brings about this decomposition at lower temperature. This is obviously due to its strong dehydrating power coupled with the tendency of oxalic acid for decarboxylation. Any formic acid that may be formed is immediately decomposed by sulphuric acid,

$$\mathrm{HCOOH \rightarrow H_2O + CO.}$$

(3) *Reducing Action.* Oxalic acid and metallic oxalates possess strong reducing properties on account of the tendency of the oxalate ion to transform itself into two carbon dioxide molecules with **loss of two electrons.**

$$\mathrm{C_2O_4^{-2} \rightarrow 2\,CO_2 + 2\,e^-}$$

For this reason, oxalic acid and oxalates, in *acid* solution, reduce potassium permanganate *quantitatively*. Both the acid itself and sodium oxalate (which can be readily obtained pure, first as the dihydrate and the second as the anhydrous salt) are used in volumetric analysis for standardizing permanganate solutions.

The reducing power of oxalic acid and its salts also render them useful as bleaching agents, for removing rust and ink stains, and in photography (*see* next section).

Expt. 2. *Tests of Oxalic Acid and Oxalates.—*

(1) Heat the substance in a dry test tube. Decomposition with evolution of CO, CO_2 and formic acid vapour (characteristic odour), takes place ; but there occurs no charring (distinction from tartaric and citric acids).

(2) Heat with concentrated sulphuric acid. The substance dissolves, giving off CO and CO_2 ; but there occurs no charring (distinction from tartaric acid).

(3) Drop potassium permanganate solution into a hot solution of the substance acidified with sulphuric acid ; decolorization with evolution of CO_2.

(4) Add silver nitrate solution to a *neutral* solution of the substance ; white precipitate soluble in dilute ammonia. On warming the solution, no reduction occurs (distinction from tartaric acid).

(5) Add calcium chloride solution to a *neutral* solution of the substance ; white crystalline precipitate, insoluble in acetic acid.

Uses. (1) Oxalic acid (also its antimony salt) is used as a mordant in dyeing and calico-printing.

(2) The acid is employed in the manufacture of inks and certain coal-tar dyes.

(3) It is also used for whitening leather and for bleaching and cleaning straw.

(4) Salts of oxalic acid find many minor uses in the arts (*see* below).

7. **Salts of Oxalic Acid.**—Only ammonium and alkali-metal oxalates are soluble in water.

Sodium oxalate, $(COONa)_2$, can be readily obtained pure, and is used as a standard in volumetric analysis.

There are three oxalates of potassium, (*i*) the normal salt, $K_2C_2O_4.H_2O$, (*ii*) the acid salt, $KHC_2O_4.H_2O$, and (*iii*) **potassium tetroxalate**, a compound formed by the combination of a molecule of the free acid with a molecule of the acid salt. It is represented by the formula $KHC_2O_4.H_2C_2O_4.2H_2O$, and is employed under the name of **salt of sorrel** for removing ink and rust stains. The salt serves to reduce the insoluble ferric tannate and gallate to soluble ferrous salts, which are washed off.

Calcium Oxalate. $CaC_2O_4.H_2O$, is insoluble in water or acetic acid, and is used for the detection and estimation of calcium and soluble oxalates.

Ferrous oxalate, which can be obtained as a yellow powder by precipitation, is used as a "developer" in photography.

Potassium ferric oxalate, $3K_2C_2O_4.Fe_2(C_3O_4)_3$, or $K_3Fe(C_2O_4)_3$, is used in *platinum printing*. This is based on the reduction of the salt to potassium ferrous oxalate on exposure to sunlight, the electrons necessary for reduction being supplied by the oxalate ion.

8. **Derivatives of Oxalic Acid.**—

Dimethyl oxalate, $(COOCH_3)_2$, is a solid (m.p. 51°, b.p. 116°). It is used in the preparation of pure methyl alcohol (page 238).

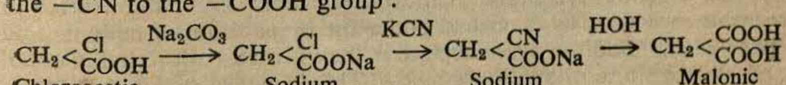
Diethyl oxalate (b.p. 186°) is employed for preparing oxalo-acetic ester.

Oxalyl chloride ClCO.COCl, (b.p. 64°) is obtained by the action of phosphorous pentachloride on anhydrous oxalic acid.

Oxamide, $NH_2CO.CONH_2$, obtained by the action of ammonia on ethyl oxalate, and **oxamic acid,** $COOH.CO.NH_2$, formed by heating ammonium acid oxalate, are respectively the di- and the mono- amides of oxalic acid.

9. **Malonic Acid.** *Methanedicarboxylic Acid, Propanedioic Acid* or *Propane Diacid*, $COOH.CH_2.COOH$.—This acid was discovered as an oxidation product of malic acid—an acid found in unripe apples (*L. malum*, apple)—and so got its name.

Preparation. Malonic acid is best prepared from chloroacetic acid by the **cyanide synthesis**. Chloroacetic acid is first converted into its sodium salt by neutralization with sodium carbonate. Sodium chloroacetate is heated with a solution of potassium cyanide in order to replace the chlorine atom by the —CN group. The resulting sodium cyanoacetate is boiled with dilute sulphuric acid to hydrolyse the —CN to the —COOH group:



$$CH_2<^{Cl}_{COOH} \xrightarrow{Na_2CO_3} CH_2<^{Cl}_{COONa} \xrightarrow{KCN} CH_2<^{CN}_{COONa} \xrightarrow{HOH} CH_2<^{COOH}_{COOH}$$

Chloroacetic acid — Sodium chloroacetate — Sodium cyanoacetate — Malonic acid

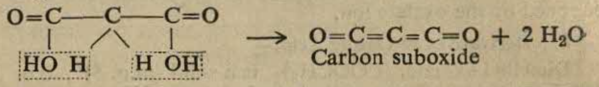
Special Properties of Malonic Acid. Special properties exhibited by this acid are due to its peculiar structure, $HOOC.CH_2.COOH$. The two carboxyl groups being linked to the same carbon atom are in close proximity. They not only impart added reactivity to each other, as in the case of oxalic acid, but also induce unusual reactivity in the hydrogen atoms of the intervening methylene group, $-CH_2-$. The following special properties of malonic acid should be looked upon in this context.

(1) *Decarboxylation.* Malonic acid, like oxalic acid, decomposes on heating somewhat above its melting point, with the evolution of carbon dioxide :—

$$\underset{\text{Malonic acid}}{H\boxed{OOC}CH_2COOH} \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

This property of decarboxylation is also shown by the mono- and the di- alkyl malonic acids, and is of considerable importance for the synthesis of certain fatty acids (page 382).

(2) *Dehydration.* Behaviour of malonic acid towards phosphorus pentoxide is most abnormal. Instead of giving a closed-chain anhydride, $H_2C{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$, as expected, it loses *two* molecules of water, giving an unusually reactive and highly unsaturated compound, called **carbon suboxide**,



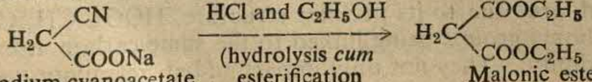
Carbon suboxide

Carbon suboxide is a gas with powerfully pungent, acrolein-like odour. It exhibits the behaviour of an acid anhydride, and combines with two molecules of water to regenerate malonic acid, and reacts with ammonia to give malonamide and with alcohol to form diethyl malonate.

(3) *Reactivity of Methylenic Hydrogen.* The formation of carbon suboxide, just described, is an instance of the reactivity of the CH_2 group induced by the two carboxyl groups attached to it. Esters of malonic acid react with sodium ethoxide to form sodio-derivatives by the replacement of methylenic hydrogen atoms by sodium. This reaction forms the basis of the use of diethyl malonate as a synthetic reagent of great importance.

10. Malonic Ester, $CH_2(COOC_2H_5)_2$. The diethyl ester of malonic acid, commonly called *malonic ester*, is one of the most important synthetic reagents in organic chemistry.

Preparation. Malonic ester is prepared from chloroacetic acid by the cyanide synthesis. Chloroacetic acid is first converted to **sodium cyanoacetate**, as described under the preparation of malonic acid (page 379). Sodium cyanoacetate is then heated with ethyl alcohol and hydrochloric or sulphuric acid. This brings about, in *one operation*, the hydrolysis of the – CN to the —COOH group and the esterification of both the carboxyl groups :—



$$H_2C{<}\begin{smallmatrix}CN\\COONa\end{smallmatrix} \xrightarrow[\text{(hydrolysis } cum \text{ esterification}]{HCl \text{ and } C_2H_5OH} H_2C{<}\begin{smallmatrix}COOC_2H_5\\COOC_2H_5\end{smallmatrix}$$

Sodium cyanoacetate (hydrolysis *cum* esterification Malonic ester

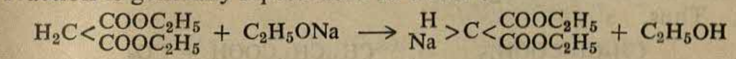
Properties Malonic ester is a colourless liquid with a faintly aromatic odour and boiling at 198°.

Malonic ester gives the usual ester reactions, involving one or both the ester groups. Its most important reactions, however, are dependent upon its peculiar structure. The close proximity of the two carbethoxyl groups intensifies the reactivity of each other. Moreover, it activates the hydrogen atoms of the intervening $—CH_2—$ group. The synthetic applications of malonic ester, discussed in the following sections may be divided into two groups :—

(*i*) Syntheses through sodio-malonic ester (sec. 11).

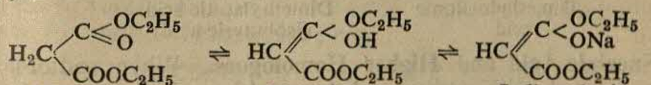
(*ii*) Syntheses without the intervention of the sodio-derivative (sec. 12).

11. Malonic Ester Syntheses involving use of Sodio-Derivative.— The hydrogen atoms of the methylene group, being under the joint activating influence of the two unsaturated carboxyl groups, are unusually reactive. They may be replaced, one after the other, by an active metal, such as sodium or potassium. Thus, when sodium ethoxide is added to a dry ethereal solution of malonic ester, a monosodio derivative, called **sodio-malonic ester**, is produced. The reaction is generally represented as under :—



$$H_2C{<}\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + C_2H_5ONa \longrightarrow \begin{matrix}H\\Na\end{matrix}{>}C{<}\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + C_2H_5OH$$

However, as a matter of fact, it is through the *enol* form that the replacement of hydrogen by sodium occurs (compare acetoacetic ester) :—



Malonic ester (keto form) ⇌ Malonic ester (enol form) ⇌ Sodiomalonic ester

Sodio-malonic ester reacts with alkyl halides, alkylene halides, esters of halogen-substituted fatty acids and acid chlorides with the result that the sodium atom is replaced by an organic radical. Most of the syntheses of malonic ester are through the sodio-derivative. The general procedure is to add the calculated quantity of the halogen compound to the alcoholic solution of sodiomalonic ester without actually isolating the latter.

We may synthesize the following classes of compounds through sodio-malonic ester :—

(1) **Mono- and Di-alkylmalonic Acids.** (*a*) When malonic ester is added to absolute alcohol in which one equivalent proportion of metallic sodium has been dissolved, **sodio-metallic ester** is produced.

$$\underset{\text{Malonic ester}}{H_2C(COOC_2H_5)_2} + \underset{\text{Sodium ethoxide}}{NaOC_2H_5} \rightarrow \underset{\text{Sodio-malonic ester}}{NaHC(COOC_2H_5)_2} + C_2H_5OH$$

This compound, when treated with one molecular proportion of an alkyl iodide, yields a mono-alkyl derivative of malonic ester ; *e.g.*,

$$NaHC(COOC_2H_5)_2 + CH_3I \rightarrow \underset{\text{Methylmalonic ester}}{(CH_3)HC(COOC_2H_5)_2} + NaI$$

The mono-alkyl malonic ester may be hydrolysed in the usual manner by means of alcoholic caustic potash, and the free acid separated by the addition of hydrochloric acid and extraction with ether.

(*b*) If, instead of hydrolysing it, the mono-alkyl malonic ester be treated with one more equivalent of sodium ethoxide, the remaining labile hydrogen atom is replaced by sodium :

$$RHC(COOC_2H_5)_2 + NaOC_2H_5 \rightarrow \underset{\text{Sodio-alkylmalonic ester}}{NaRC(COOC_2H_5)_2} + C_2H_5OH$$

Upon treating the sodio-derivative, thus obtained, with an equivalant proportion of an alkyl iodide (which may be the same as used previously, or a different one), a di-alkyl malonic ester is produced :

$$NaRC(COOC_2H_5)_2 + R'I \rightarrow \underset{\text{Dialkylmalonic ester}}{{}^{R'}_{R}\!>C(COOC_2H_5)_2} + NaI$$

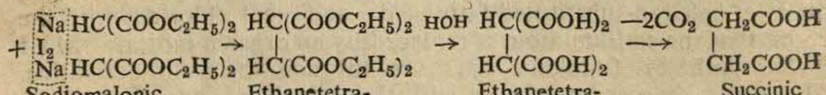
This may by converted into the free acid as before.

(2) **Mono- and Dialkylacetic Acids.** Mono- and di-alkyl malonic acids, like malonic acid itself, lose carbon dioxide on heating and pass into the corresponding **fatty acids**, *viz.* mono- and dialkylacetic acids. Thus,

$$\underset{\substack{\text{Methyl-malonic}\\ \text{acid}}}{CH_3CH(COOH)_2} \rightarrow \underset{\substack{\text{Methylacetic acid}\\ \text{(Propionic acid)}}}{CH_3.CH_2.COOH} + CO_2$$

$$\underset{\substack{\text{Dimethylmalonic}\\ \text{acid}}}{(CH_3)_2C(COOH)_2} \rightarrow \underset{\substack{\text{Dimethylacetic acid}\\ \text{(Isobutyric acid)}}}{(CH_3)_2CHCOOH} + CO_2$$

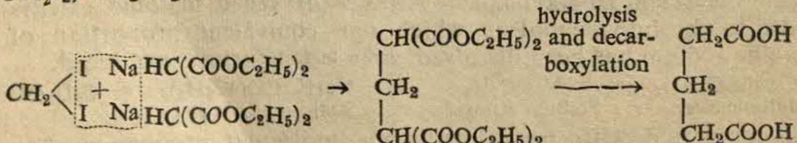
(3) **Succinic Acid and Higher Homologues.** When sodiomalonic ester is treated with iodine and the resulting ethane tetracarboxylic ester submitted to hydrolysis followed by decarboxylation, we get succinic acid :—



$$\begin{array}{l} Na\,HC(COOC_2H_5)_2\\ +\,I_2\\ Na\,HC(COOC_2H_5)_2 \end{array} \rightarrow \begin{array}{l} HC(COOC_2H_5)_2\\ |\\ HC(COOC_2H_5)_2 \end{array} \xrightarrow{HOH} \begin{array}{l} HC(COOH)_2\\ |\\ HC(COOH)_2 \end{array} \xrightarrow{-2CO_2} \begin{array}{l} CH_2COOH\\ |\\ CH_2COOH \end{array}$$

Sodiomalonic ester (2 mols) Ethanetetra-carboxylic acid Ethanetetra-carboxylic acid Succinic acid

If, instead of iodine, we use a dihalogen alkane derivative having halogen atoms in the end positions of the carbon chain, we get higher members of the oxalic acid series. Thus, by using di-iodomethane, CH_2I_2, we get glutaric acid :—



$$CH_2\!\left\langle \begin{array}{l} I\;\;Na\,HC(COOC_2H_5)_2\\ +\\ I\;\;Na\,HC(COOC_2H_5)_2 \end{array}\right. \rightarrow \begin{array}{l} CH(COOC_2H_5)_2\\ |\\ CH_2\\ |\\ CH(COOC_2H_5)_2 \end{array} \xrightarrow{\substack{\text{hydrolysis}\\ \text{and decar-}\\ \text{boxylation}}} \begin{array}{l} CH_2COOH\\ |\\ CH_2\\ |\\ CH_2COOH \end{array}$$

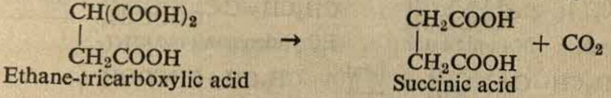
Propanetetracarboxylic ester Glutaric acid

Similarly, the use of $BrCH_2.CH_2Br$ and $BrCH_2.CH_2.CH_2Br$, results in the formation of adipic and pimelic acids.

(4) **Succinic and Alkyl-succinic Acids.** When sodio-malonic ester is treated with chloroacetic ester, we get ethane-tricarboxylic ester :

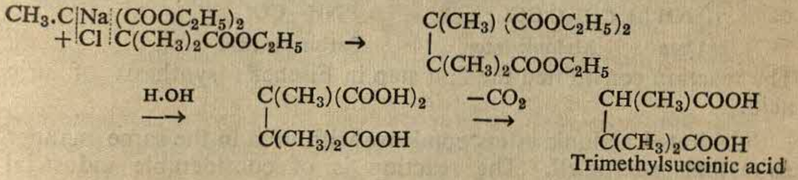
$$\underset{\text{Sodio-malonic ester}}{(COOC_2H_5)_2CH\,Na} + \underset{\text{Chloroacetic ester}}{Cl\,CH_2COOC_2H_5} \rightarrow \underset{\text{Ethane-tricarboxylic ester}}{(COOC_2H_5)_2CH.CH_2COOC_2H_5} + NaCl$$

This, when hydrolysed, yields the corresponding acid, which on heating, loses a molecule of carbon dioxide, producing succinic acid:



$$\underset{\text{Ethane-tricarboxylic acid}}{\begin{array}{c}CH(COOH)_2\\ |\\ CH_2COOH\end{array}} \rightarrow \underset{\text{Succinic acid}}{\begin{array}{c}CH_2COOH\\ |\\ CH_2COOH\end{array}} + CO_2$$

By using sodio-alkylmalonic esters and mono- and di-alkyl chloroacetic esters in the synthesis, alkylsuccinic acids can be obtained. This gives us a method of **passing from the malonic acid series to the succinic acid series.** Thus trimethylsuccinic acid may be obtained from sodio-methylmalonic ester and dimethyl-chloroacetic ester as shown below :



$$\begin{array}{l}CH_3.C\,Na\,(COOC_2H_5)_2\\ +Cl\,C(CH_3)_2COOC_2H_5\end{array} \rightarrow \begin{array}{l}C(CH_3)\,(COOC_2H_5)_2\\ |\\ C(CH_3)_2COOC_2H_5\end{array}$$

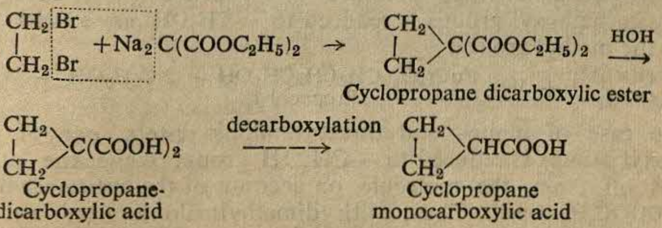
$$\xrightarrow{H.OH} \begin{array}{l}C(CH_3)(COOH)_2\\ |\\ C(CH_3)_2COOH\end{array} \xrightarrow{-CO_2} \underset{\text{Trimethylsuccinic acid}}{\begin{array}{l}CH(CH_3)COOH\\ |\\ C(CH_3)_2COOH\end{array}}$$

(5) **Keto Acids.** Sodiomalonic ester reacts with acid chlorides with the formation of keto-acids ; *e.g.*,

$$\underset{\text{Acetyl chloride}}{CH_3CO\,Cl} + \underset{\text{Sodio-malonic ester}}{Na\,CH(COOC_2H_5)_2} \rightarrow \underset{\text{Acetomalonic ester}}{CH_3COCH(COOC_2H_5)_2}$$

$$\xrightarrow{\text{Hydrolysis}} \underset{\text{Acetomalonic acid}}{CH_3COCH(COOH)_2} \xrightarrow{\text{decarboxylation}} \underset{\text{Acetoacetic acid}}{CH_3COCH_2COOH}$$

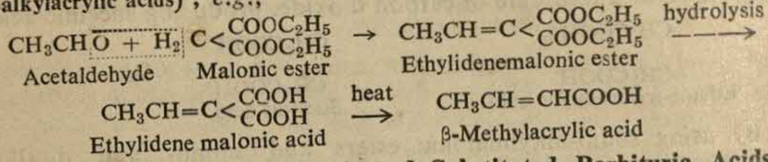
(6) **Cycloparaffin Carboxylic Acids.** Dihalogen alkane derivatives having the halogen atoms in the end positions of the carbon chain react with disodiomalonic ester, yielding cycloparaffin carboxylic acids ; *e.g.*,


CH₂Br
CH₂Br
+Na₂C(COOC₂H₅)₂
CH₂
CH₂
C(COOC₂H₅)₂
HOH
Cyclopropane dicarboxylic ester
CH₂
CH₂
C(COOH)₂
decarboxylation
CH₂
CH₂
CHCOOH
Cyclopropane-dicarboxylic acid
Cyclopropane monocarboxylic acid

Similarly, 1,3-dibromopropane, $BrCH_2.CH_2.CH_2Br$, and 1,4-dibromobutane, $BrCH_2.CH_2.CH_2.CH_2Br$, give cyclobutane- and cyclopentane-carboxylic acids.

12. Other Malonic Ester Syntheses.—There are a number of syntheses in which malonic ester reacts directly. The more important of these are :—

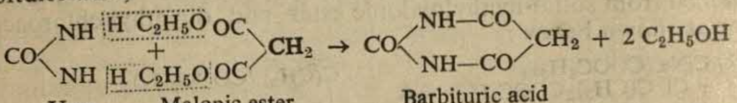
(1) **Synthesis of $\triangle^2$-Unsaturated Acids.** Malonic ester undergoes **condensation with aldehydes** in the presence of an organic base (such as piperidine). The alkylidene malonic esters, thus produced, on hydrolysis followed by decarboxylation, give $\triangle^2$-unsaturated acids **(β-alkylacrylic acids)** ; *e.g.*,



$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}} + \underset{\text{Malonic ester}}{\mathrm{H_2C}\Big<\substack{\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}}} \rightarrow \underset{\text{Ethylidenemalonic ester}}{\mathrm{CH_3CH{=}C}\Big<\substack{\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}}} \xrightarrow{\text{hydrolysis}}$$

$$\underset{\text{Ethylidene malonic acid}}{\mathrm{CH_3CH{=}C}\Big<\substack{\mathrm{COOH}\\ \mathrm{COOH}}} \xrightarrow{\text{heat}} \underset{\text{β-Methylacrylic acid}}{\mathrm{CH_3CH{=}CHCOOH}}$$

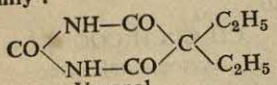
(2) **Synthesis of Barbituric Acid and Substituted Barbituric Acids.** Malonic ester undergoes **condensation with urea** to give malonyl urea or barbituric acid,



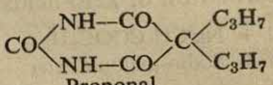
Urea Malonic ester Barbituric acid

The reaction constituted the first step in Fischer's synthesis of uric acid.

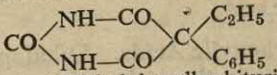
Substituted malonic esters condense with urea in the same manner as malonic ester itself. The reaction is of considerable industrial importance, as it is employed in the **manufacture of hypnotic drugs of veronal family** :—



Veronal
(Diethylbarbituric acid)

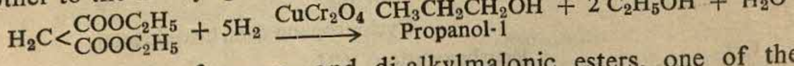


Proponal
(Dipropylbarbituric acid)



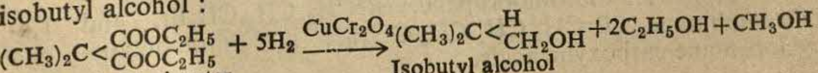
Luminal (Ethylphenylbarbituric acid)

(3) **Synthesis of Primary Alcohols.** When malonic ester is heated with hydrogen under high pressure over cupric chromite catalyst, one of its carbethoxyl groups is reduced to —CH_2OH **group** and the other to the methyl group :



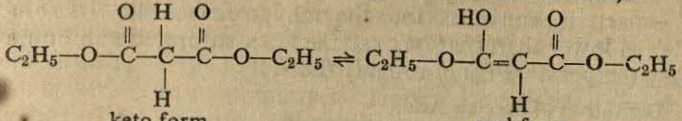
$$\mathrm{H_2C}\Big<\substack{\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}} + 5\mathrm{H_2} \xrightarrow{\mathrm{CuCr_2O_4}} \underset{\text{Propanol-1}}{\mathrm{CH_3CH_2CH_2OH}} + 2\,\mathrm{C_2H_5OH} + \mathrm{H_2O}$$

In the case of mono- and di-alkylmalonic esters, one of the carbethoxyl groups is reduced to —CH_2OH group, while the other separates off from the molecule on account of the **hydrogenolysis of the C—$COOC_2H_5$ bond.** Thus, with dimethylmalonic ester we get isobutyl alcohol :



$$\underset{\text{Dimethylmalonic ester}}{\mathrm{(CH_3)_2C}\Big<\substack{\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}}} + 5\mathrm{H_2} \xrightarrow{\mathrm{CuCr_2O_4}} \underset{\text{Isobutyl alcohol}}{\mathrm{(CH_3)_2C}\Big<\substack{\mathrm{H}\\ \mathrm{CH_2OH}}} + 2\mathrm{C_2H_5OH} + \mathrm{CH_3OH}$$

13. Keto-Enol Tautomerism of Malonic Ester.—Malonic ester exhibits keto-enol tautomerism (compare Acetoacetic ester).



$$C_2H_5-O-\overset{O}{\overset{\|}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \rightleftharpoons C_2H_5-O-\overset{HO}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

keto form enol form

but the equilibrium lies close to 100 per cent of the keto form. Of the three recognized tests for the existence of the enol form, *viz.*,

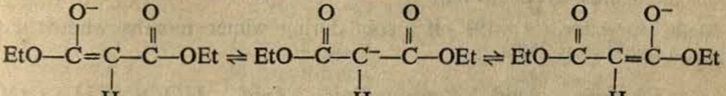
(1) dissolution of the substance in *alcoholic* sodium ethoxide,

(2) colour reaction with ferric chloride,

(3) bromine-addition,

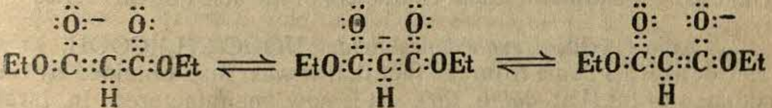
malonic ester responds to the first only. This is because of the point of equilibrium lying almost entirely on the side of the keto form. However, when sodiomalonic ester is acidified and the ferric chloride and the bromine tests applied *immediately*, both these are found to be positive. On allowing to stand, the enol form changes to the keto form almost completely and the enol-form concentration falls to such a low point that the existence of the enol form becomes undetectable by tests (2) and (3).

Sodiomalonic ester ionizes, as other salts do, and the anion resonates between the three hybrid structures :—



$$EtO-\overset{O^-}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-\overset{O}{\overset{\|}{C}}-OEt \rightleftharpoons EtO-\overset{O}{\overset{\|}{C}}-\underset{\underset{H}{|}}{C^-}-\overset{O}{\overset{\|}{C}}-OEt \rightleftharpoons EtO-\overset{O}{\overset{\|}{C}}-\underset{\underset{H}{|}}{C}=\overset{O^-}{\overset{|}{C}}-OEt$$

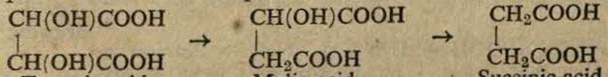
The electronic representation is as under :—



$$EtO:\overset{:\ddot{O}:^-}{C}::\underset{\ddot{H}}{C}:\overset{\ddot{O}:}{\ddot{C}}:OEt \rightleftharpoons EtO:\overset{:\ddot{O}}{\ddot{C}}:\underset{\ddot{H}}{\overset{-}{\ddot{C}}}:\overset{\ddot{O}:}{\ddot{C}}:OEt \rightleftharpoons EtO:\overset{\ddot{O}:}{\ddot{C}}:\underset{\ddot{H}}{C}::\overset{:\ddot{O}:^-}{C}:OEt$$

14. Succinic Acid. *Butanedioic Acid*, or *Ethane dicarboxylic Acid*, $HOOC.CH_2.CH_2.COOH$.—This acid occurs in amber (Lat. *succinum*), from which source it was first obtained by distillation.

Preparation. The most important method of preparation is by the fermentation of calcium malate (or of ammonium tartrate) by yeast or putrid cheese. The process is one of reduction :



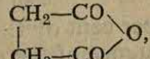
$$\begin{array}{c}CH(OH)COOH\\|\\CH(OH)COOH\end{array} \rightarrow \begin{array}{c}CH(OH)COOH\\|\\CH_2COOH\end{array} \rightarrow \begin{array}{c}CH_2COOH\\|\\CH_2COOH\end{array}$$

Tartaric acid Malic acid Succinic acid

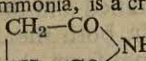
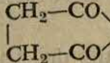
Synthesis. Succinic acid may be *synthesized* from (*i*) ethylene cyanide or β-iodopropionic acid, (*ii*) ethyl potassium malonate by electrolysis and (*iii*) malonic ester.

Properties. Succinic acid crystallizes in colourless prisms, m.p. 185°. It sublimes readily, giving off irritating vapour. When distilled, it is partially converted into the anhydride (sec. 4). Its solubility in water is lower than that of oxalic acid, a saturated solution at the ordinary temperature being roughly 0·8N.

15. Derivatives of Succinic Acid.

Succinic anhydride,  $\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array} > O$, is prepared by heating the acid with phosphorus pentoxide or phosphorus oxychloride for some time, and distilling the product. It is a colourless, crystalline substance, *m.p.* 120°. When boiled with water, it passes into succinic acid.

Succinyl Chloride, $(CH_2COCl)_2$, produced by the action of phosphorus pentachloride on succinic acid, is a colourless liquid, *b.p.* 190°. It has the usual characters of an acid chloride.

Succinamide, $(CH_2CONH_2)_2$. obtained by the interaction of ethyl succinate and concentrated ammonia, is a crystalline solid, *m.p.* 242°. On heating, it passes into **succinimide,**[1]  $\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array} > NH$, *m.p.* 126°. This latter substance is *acidic* in character, the hydrogen of the >NH group being replaceable by metals. Thus when alcoholic solutions of succinimide and caustic potash are mixed together, *potassium succinimide,*  $\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array} > NK$, is obtained as crystals. The reactivity of the hydrogen of the >NH group is due to its situation between two —CO— groups (compare ethyl malonate).

Methyl succinate, (*m.p.* 193°) is a solid during winter months while the **ethyl ester** is a liquid (*b.p.* 280°).

16. Glutaric Acid, *Pentanedioic Acid,* $HOOC(CH_2)_3COOH$, *m.p.* 97°, may be synthesized from trimethylene bromide, $BrCH_2CH_2CH_2Br$, by the cyanide method, or by the malonic ester synthesis. It shows the usual characters of the acids of this series.

17. Adipic Acid, *Hexanedioic Acid.* $HOOC(CH_2)_4COOH$, *m.p.* 153°, derives its name from the fact that it was first obtained by the oxidation of fat (Lat. *adipis*, fat). It is now manufactured in large quantities for the manufacture of Nylon by the oxidation of cyclohexanol (obtained from phenol by catalytic hydrogenation) or of cyclohexane (which occurs in large quantities in Russian petroleum) with 65 per cent nitric acid.

18. Nylon.—This is a **synthetic silk** obtained by heating adipic acid with hexamethylene diamine :—

$$\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{H_2N(CH_2)_6NH_2} \rightarrow \text{Polymeride} \xrightarrow{\text{cold drawing}} \text{Nylon}$$

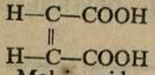
---

[1] Hence it is not possible to prepare succinamide, by the action of heat on ammonium succinate, succinamide being produced instead.

The resulting polyamide has a high molecular weight (10,000 to 25,000). It melts at about 260° and the molten material, when drawn, yields fine threads. This can be stretched at the room temperature (“**cold drawing**”) to four times their original length, but, unlike an elastic material, no contraction occurs when the stretching force is removed. The fibre resembles silk in having lustre and high tensile strength, and is used as a textile, especially in the manufacture of underwear, women’s stockings, jungle clothing, and parachutes. The attractive summer dresses made of nylon can be washed and dried in less than an hour. Nylon is also used in making toothbrush bristles.

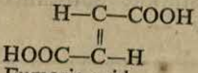
II. UNSATURATED DIBASIC ACIDS

19. Olefine Dicarboxylic Acids.—The dibasic acids derived from olefine hydrocarbons possess the dual character of (*i*) a dibasic acid, and (*ii*) an olefinic compound. The following are the better-known members of this group, the first four of which exhibit geometrical isomerism :—



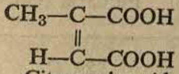
$$\begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Maleic acid



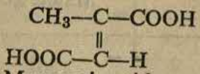
$$\begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{HOOC{-}C{-}H}\end{array}$$

Fumaric acid



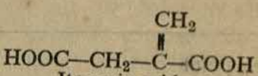
$$\begin{array}{c}\mathrm{CH_3{-}C{-}COOH}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Citraconic acid



$$\begin{array}{c}\mathrm{CH_3{-}C{-}COOH}\\ \|\\ \mathrm{HOOC{-}C{-}H}\end{array}$$

Mesaconic acid



$$\begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{HOOC{-}CH_2{-}C{-}COOH}\end{array}$$

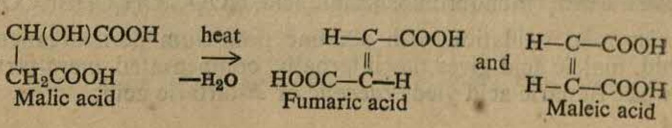
Itaconic acid

Maleic acid and fumaric acid are the *cis*-form and the *trans*-form respectively of **ethylenedicarboxylic acid.** Citraconic acid is the *cis*-form of **methylethylenedicarboxylic acid** and mesaconic acid is its *trans*-form. Itaconic acid is **methylenesuccinic acid**, and is isomeric with citraconic and mesaconic acids. It does *not* exhibit geometrical isomerism.

Maleic and fumaric acids are both obtained by the action of heat on maleic acid, while the other three are obtainable by heating citric acid under different conditions.

20. Maleic Acid and Fumaric Acid (*cis* and *trans* Ethylenedicarboxylic Acids). These two acids afford the best known example of geometrical isomerism. Fumaric acid occurs in certain plants, especially toadstools and *fumaria officinalis.* Maleic acid does *not* occur in nature.

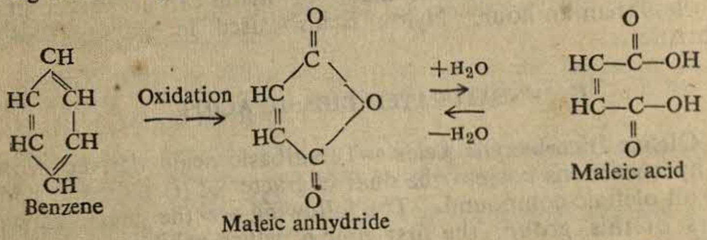
Preparation. Both these acids may be obtained by heating malic acid :—



$$\begin{array}{c}\mathrm{CH(OH)COOH}\\ |\\ \mathrm{CH_2COOH}\end{array} \xrightarrow[-\mathrm{H_2O}]{\text{heat}} \begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{HOOC{-}C{-}H}\end{array} \text{ and } \begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Prolonged heating at 140°—150° gives fumaric acid as the principal product. At higher temperatures, a distillate consisting mainly of maleic *anhydride* and water is obtained. The anhydride readily takes up water, yielding maleic acid.

Manufacture. Maleic acid and its anhydride find extensive use in the production of alkyd resins. They are prepared in considerable quantities by catalytic oxidation of benzene with air, the anhydride being the main product :—



Physical Properties. Maleic acid and fumaric acid are both colourless, crystalline substances. Their physical constants are tabulated below :--

	Maleic acid	Fumaric acid
Melting point	130°	287°C
Boiling point	160° (decom.)	200° (sublimes)
Solubility, gm./100 ml. water (at 25°C)	79	0.7
Specific gravity	1.600	1.635
Heat of combustion, kilo-cal/mole	327	320
Primary ionization constant, $K \times 10^{-2}$	1.170	0.093

Chemical Properties. Except for the phenomenon of geometrical isomerism and a few differences dependent thereon, maleic and fumaric acids are remarkably similar in chemical behaviour. Both of them exhibit the usual acid properties as well as the typical double-bond reactions, yielding in most cases, identical or similar products ; *e.g.*,

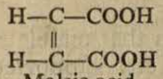
(1) They both react with alkalis and alcohols to form their respective salts and esters.

(2) On hydrogenation, both of them give succinic acid, $HOOCCH_2CH_2COOH$.

(3) On treatment with bromine, they both give the same dibromosuccinic acid, HOOC.CHBr.CHBr.COOH, and with hydrogen bromide the same monobromosuccinic acid, $HOOC.CH_2CHBr.COOH$.

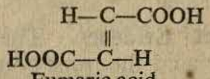
(4) On mild oxidation with alkaline potassium permanganate in the cold, maleic acid gives the internally compensated *meso*-tartaric acid, while fumaric acid yieds *racemic* or *dl*-tartaric acid.

21. Geometrical Isomerism of Maleic and Fumaric Acids.— The close similarity in most of the reactions of the two acids clearly shows that they possess the same structural formula, *viz.*, HOOCCH=CHCOOH. The difference in physical properties and some chemical reactions is due to the difference in spatial arrangement of the atoms or groups attached with the doubly bound carbon atoms, *i.e.*, to geometrical isomerism. As the result of careful study of these differences, maleic acid has been assigned the *cis-* and fumaric acid the *trans*-formula:



$$\begin{array}{c}\text{H—C—COOH}\\ \|\\ \text{H—C—COOH}\end{array}$$

Maleic acid
(*cis*)

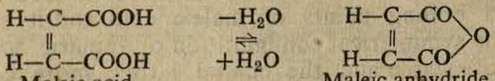


$$\begin{array}{c}\text{H—C—COOH}\\ \|\\ \text{HOOC—C—H}\end{array}$$

Fumaric acid
(*trans*)

We may here summarize the evidence on which the assignment of these formulae is based.

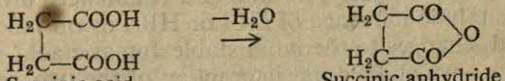
(1) **Anhydride Formation.** When maleic acid is heated, it yields a cyclic anhydride, which, in its turn, takes up water under mild conditions with the regeneration of maleic acid :



Maleic acid
Maleic anhydride

Fumaric acid loses water only when heated *very strongly*, producing some *maleic* anhydride ; no fumaric anhydride is formed at all. It is but natural to believe that the anhydride formation, by loss of water between the two carboxyl groups, would more easily occur the nearer they are to each other. So, maleic acid was assigned the *cis-* and fumaric acid the *trans*-formula.

(2) **Correlation with Succinic Acid.** Succinic acid, to which maleic and fumaric acids are related in skeletal structure, readily yields a cyclic anhydride,

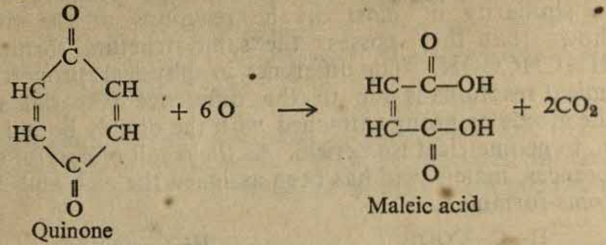


Succinic acid
Succinic anhydride

A reference to Fig. 6 on page 71 will show that in a 4 carbon chain, atoms and groups attached to the end carbons are quite near each other, so that if they are capable of reacting together they will readily do so. That is, the position is very favourable for cyclization. Since maleic acid and succinic acid both readily give cyclic anhydrides, and since in succinic acid the two carboxyls are known to be very near each other, they must be close together in the case of maleic acid also. That is, maleic acid must possess the *cis* configuration and fumaric acid, which is incapable of andydride formation, must be the *trans* compound.

(3) **Correlation with Quinone.** The fact that quinone gives

maleic acid on oxidation also indicate the *cis* formula for maleic acid,



(4) **Physical Evidence.** The conclusion that maleic acid is the *cis* and fumaric acid the *trans* compound is fully supported by physical properties of the two acids (*see* table of physical constants on p. 388). The close proximity of the two carboxyl groups in maleic acid makes them exert strong inductive influence on each other. This accounts for the very high ionization constant of this acid as compared with that of fumaric acid. The crowding together of bulky carboxyl groups on the same side of the molecule produces in it a lack of symmetry and a less harmonious, and therefore less compact, packing of molecules in the crystal. This is in accord with the lower melting and boiling points of maleic acid and its smaller specific gravity. The symmetrical configuration of fumaric acid makes the molecule more stable and the crystal lattice more compact. This accounts for its considerably higher melting and boiling points, higher density and very small solubility in water.

22. Interconversion of Maleic and Fumaric Acids.—Under the influence of heat and certain chemical reagents, the double bond gets weakened to such an extent that rotation becomes possible, and the cis-trans interconversion occurs, until a state of equilibrium is established :

$$\text{cis-form} \rightleftharpoons \text{trans-form}$$

The point of equilibrium, of course, will depend on the conditions imposed, and is subject to the Le Chatelier principle. Thus, under the catalytic influence of HCl or HBr, or on moderate heating, maleic acid changes to the more stable fumaric acid. At very high temperatures, which favours interaction of the two carboxyl groups with the production of *maleic* anhydride, the equilibrium persistently shifts to the left and fumaric acid changes to maleic acid and thence to maleic anhydride.

Maleic acid is richer in energy than fumaric acid, as the more unstable geometrical isomers always are. Its higher heat of combustion (327 kilo-cals against 320 of fumaric acid) is a clear proof of the higher energy content of maleic acid. Hence, if energy level of the system be raised, the equilibrium will be shifted in favour of the isomer with higher energy content. Thus, when an aqueous solution of fumaric acid is irradiated with ultra-violet light at 50°, a condition of equilibrium is set up within a few hours with 75 per cent conversion of fumaric to maleic acid.

Cis-trans interconversion also occurs in the case of maleic and fumaric acid derivatives. Thus diethyl maleate is rapidly converted into diethyl fumarate in the presence of a trace of iodine.

QUESTIONS

1. Give the general methods of formation and properties of dicarboxylic acids of the oxalic acid series. Describe the peculiarities that these acids exhibits depending on (*i*) the number of carbon atoms in the molecule, and (*ii*) the number of carbon atoms separating the two carboxyl groups from each other.

2. A dibasic acid containing only carbon, hydrogen and oxygen was found by analysis to contain C=26·7 per cent ; H=2·2 per cent. A determination of the vapour density of its dimethyl ester gave $\triangle=59$. What is the acid ?

Ans. Oxalic acid, HOOC.COOH.

3. Outline a method for the commercial preparation of oxalic acid. Name two of its important salts, and give their uses. Starting from oxalic acid, how would you prepare ethyl oxalate and formic acid ? (*Calcutta, B.Sc., 1954*)

4. Give an account of the chemistry of maleic and fumaric acids, and discuss fully the geometrical isomerism of these acids. (*Mysore, B.Sc., 1953*)

5. Give the synthetic uses of malonic ester. (*Lucknow, B.Sc., 1959, 1961*)

6. Outline a method for the preparation of oxalic acid on a commercial scale. Mention the names of two of its important salts and their uses. Starting from oxalic acid how would you prepare ethyl oxalate and formic acid ? Write equations. (*Calcutta, B.Sc., 1954*)

7. Give the relationship between (1) succinic acid, (2) malic acid, (3) maleic acid and (4) fumaric acid. Describe how succinic acid can be converted into malic acid and malic acid into maleic and fumaric acids. Discuss the structure of maleic and fumaric acids. (*Poona, B.Sc., 1955*)

8. Give reactions which suggest that succinic acid is a dibasic acid. How can it be synthesised ? In what respects does succinic acid differ from oxalic acid and malonic acid ? (*Punjab, B.Sc., 1962*)

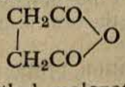
9. Discuss fully the configurations of maleic and fumaric acids and their interconvertibility. (*Madras, B Sc., 1962*)

10. On combustion, 0·118 gm. of an acid, X, containing only carbon, hydrogen and oxygen, gave 0·176 gm. of carbon dioxide and 0·054 gm. of water. Its ethyl ester has a density of 87. X, on heating, evolves carbon dioxide, leaving a strongly acid liquid. What is the probable constitution of X and that of the product formed on heating ? (*Punjab, B.Sc., 1963*)

11. Describe the preparation and synthetic applications of malonic ester. (*Gujarat, B.Sc., 1959*)

12. On combustion 0·25 g. of a neutral compound gave 0·44 g. of CO_2 and 0·09 gm. of H_2O. It dissolved slowly in boiling water giving an acid solution. On neutralizing the solution and adding silver nitrate, a silver salt was formed which was found to contain 65·1% Ag and to be derived from a dibasic acid. Deduce the molecular formula and write its structural formula. (*Agra, B.Sc., 1957*)

Ans. $C_4H_4O_3$; Succinic anhydride,



$$\begin{array}{l} CH_2CO \\ | \qquad\quad \rangle O \\ CH_2CO \end{array}$$

13. Describe the preparation of diethyl malonate. Illustrate, with suitable examples, the use of diethyl malonate in organic synthesis (*Bombay, B.Sc., Chemistry, Subs., 1962*)

14. Describe the preparation and synthetic uses of ethyl malonate. (*Agra, B Sc., 1959*)

15. A solid organic acid was found to have the empirical formula CHO. The silver salt contained 65% of silver and V. D. of its neutral ethyl ester was 86. On treatment with a solution of Br_2 in chloroform in the cold, it readily formed

a crystalline bromo-derivative containing 58% of bromine. Work out the probable constitutional formula of the acid. (*Nagpur, B.Sc., 1953*)

Ans. $COOH.CH{=}CH.COOH$.

16. A dibasic acid gave the following results on analysis :

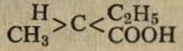
(*a*) 0·236 gm. of the acid gave 0·352 gm. CO_2 and 0·108 gm. H_2O.

(*b*) 0·177 gm. of acid required 30 c.c. N/10 NaOH for neutralization. Write down the possible structural formula of the acid. What experiments would you perform to assign it a definite structure ? (*Agra, B.Sc., 1956*)

Ans. $COOH.CH_2.CH_2.COOH$, *or* $COOH.CH(CH_3).COOH$.

17. An optically active monobasic acid contains C=58·82, H=9·8%. On incineration, 0·2299 gm. of its silver salt yields 0·1188 gm. of silver. The compound can be synthesised from malonic ester. What conclusions would you draw from the foregoing data with regard to its constitution ? (*Punjab, B.Sc., 1956*)

Ans.



$$\begin{matrix}H\\CH_3\end{matrix}{>}C{<}\begin{matrix}C_2H_5\\COOH\end{matrix}$$

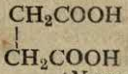
18. How is diethyl malonate prepared ? Give an account of its synthetic applications. (*Travancore, B.Sc., 1951*)

19. What do you understand by *reactive* methylene group ? Give an account of the preparation of diethyl malonate and its uses as a synthetic reagent. (*Banaras, B.Sc., 1956*)

20. How is pure diethyl malonate obtained ia the laboratory Starting from this compound how would you prepare the following substances :—

(*i*) $R_1R_2CH.COOH$

(*ii*)



$$\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$$

(*iii*) $RCH{=}CHCOOH$

(*Nagpur, B.Sc., 1957*)

21. Give an account of the synthetic uses of diethyl malonate. (*Allahabad, B.Sc., 1959*)

22. Discuss the methods of preparation and synthetic uses of Malonic ester. (*Punjab, Pakistan, B.Sc., 1958*)

23. Describe important stages in the preparation of ethyl malonate from acetic acid. Illustrate the use of this compound in the preparation of :

(*a*) Propionic acid. (*b*) Succinic acid. (*c*) Barbituric acid.

(*Rajasthan, B.Sc., 1958*)

24. Give an account of the preparation of amino-acids from natural sources and by synthetic methods. Discuss the structure of glycine. What is the effect of heat on α, β and γ amino-acids ? (*Kerala, B.Sc., 1958*)

25. How is diethylmalonate prepared ? Starting with diethylmalonate, how would you prepare (*a*) glutaric acid (*b*) propionic acid and (*c*) 1 : 2, dimethyl succinic acid ? (*Allahabad, B.Sc., 1959*)

26. Give an account of the synthetic uses of malonic ester. Give also its preparation. (*Jammu & Kashmir, B.Sc., 1959*)

27. Indicate the steps in the preparation of ethyl malonate from acetic acid. Illustrate, giving equations, the typical uses of ethyl malonate in organic synthesis. (*Utkal, B.Sc., 1960*)

28. Discuss the preparation, properties and synthetic applications of malonic ester. (*Mysore, B.Sc., 1960*)

29. Mention the compounds that contain a reactive methylane group and describe the synthetic uses of malonic ester. (*Aligarh, B.Sc., 1960*)

30. Describe the preparation of diethyl malonate. How can it be used for the synthesis of the following :—

(*a*) Dimethylacetic acid ; (*b*) Methylsuccinic acid ;
(*c*) Crotonic acid ; (*d*) Glutaric acid ?

(*Gorakhpur, B.Sc., 1961*)

CHAPTER TWENTY-FOUR

HYDROXYCARBOXYLIC ACIDS

1. A **hydroxy acid** is derived from a carboxylic acid by the replacement of one or more hydrogen atoms of the carbon chain by hydroxyl groups. It possesses therefore the characters of an alcohol as well as of a carboxylic acid. The two methods of naming halogen-substituted acids (page 339) also apply here.

I. MONOCARBOXYLIC HYDROXY ACIDS

2. The following are the most important monocarboxylic hydroxy-acids :—

$CH_2(OH)COOH$	$CH_3CH(OH)COOH$	$CH_2(OH)CH_2COOH$
Hydroxyacetic acid	α-Hydroxypropionic acid	β-Hydroxypropionic acid
(Glycolic acid)	(Lactic acid)	(Hydracrylic acid)

3. Methods of Formation.—The monocarboxylic hydroxy-acids can be synthesized by introducing (*i*) the OH group, (*ii*) the COOH group, or (*iii*) both the groups at the same time, into the molecule of a substance. We have thus three different kinds of methods :—

(1) **By the Introduction of OH Group.**

(*i*) Starting with a carboxylic acid, we can obtain an **alpha-hydroxy-acid** in the following two steps :—

(*a*) The carboxylic acid is first converted into a chloro-substituted acid (page 339).

(*b*) The resulting chloro-acid is then boiled with water, when the chlorine atom is replaced by the hydroxyl group ; *e.g.*,

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + H_2O \rightarrow \underset{\text{Hydroxyacetic acid}}{CH_2(OH)COOH} + HCl$$

(*ii*) Starting with an amino-acid, we can obtain a hydroxy-acid by treatment with nitrous acid ; *e.g.*,

$$\underset{\text{Aminoacetic acid}}{CH_2(NH_2)COOH} + HNO_2 \rightarrow \underset{\text{Hydroxyacetic acid}}{CH_2(OH)COOH} + N_2 + H_2O$$

(*iii*) We may also synthesize hydroxy-acids by the reduction of aldehydic or ketonic acids ; *e.g.*,

$$\underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + 2H \rightarrow \underset{\alpha\text{-Hydroxypropionic acid}}{CH_3.CH(OH).COOH}$$

(2) **By the Introduction of COOH Group.** Hydroxy acids may be obtained by careful oxidation of polyhydric alcohols or of aldols[1] ;

---

[1] Since aldehydes readily undergo aldol condensation, it is possible to convert an aldehyde into a hydroxy-acid containing twice as many carbon atoms as the aldehyde itself.

e.g.,

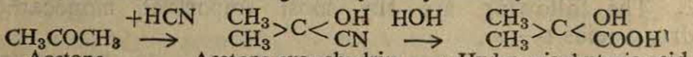
$$\underset{\text{Glycol}}{CH_2OHCH_2OH} + 2O \xrightarrow{\text{dil. } HNO_3} \underset{\text{Glycolic acid}}{CH_2(OH)COOH} + H_2O$$

$$\underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO} + O \rightarrow \underset{\beta\text{-Hydroxybutyric acid}}{CH_3CH(OH)CH_2COOH}$$

(3) **By the Introduction of both the OH and the COOH Groups.** This is effected by the addition of hydrogen cyanide to an aldehyde or a ketone, and hydrolysing the resulting cyanohydrin. Thus, starting with acetaldehyde we may obtain lactic acid (α-hydroxypropionic acid) :—

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{+HCN} \underset{\text{Acetaldehyde cyanohydrin}}{CH_3CH(OH)CN} \xrightarrow{HOH} \underset{\text{Lactic acid}}{CH_3CH(OH)COOH}$$

Similarly, from acetone we get α-hydroxy-isobutyric acid :—



$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{+HCN} \underset{\text{Acetone cyanohydrin}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CN\end{matrix}} \xrightarrow{HOH} \underset{\alpha\text{-Hydroxyisobutyric acid}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\COOH\end{matrix}}$$

Acetone Acetone cyanohydrin α-Hydroxyisobutyric acid

4. **Physical Properties** —(1) The monocarboxylic hydroxy acids are colourless, crystalline solids, or syrupy liquids, very readily soluble in water. Their boiling points are much higher than those of the corresponding fatty acids. They cannot be distilled under atmospheric pressure without decomposition.

The introduction of the hydroxyl group into the molecule increases the reactivity of the carboxyl group. Hydroxy acids, therefore, are more strongly dissociated in aqueous solution than the corresponding fatty acids (compare halogen-substituted acids).

The ionization constants of a few hydroxy acids are compared with the corresponding fatty acids in the following table :—

		$k \times 100{,}000$
Acetic acid,	CH_3COOH	1·86
Glycolic acid,	$CH_2(OH)COOH$	15·2
Propionic acid,	CH_3CH_2COOH	1·38
α-hydroxypropionic acid,	$CH_3CH(OH)COOH$	13·8
β-hydroxypropionic acid,	$CH_2(OH)CH_2COOH$	3·1

5. **Chemical Properties.**—The reactions of the hydroxy acids may be studied under four different heads :—

(1) **Reactions of Hydroxyl Group :—**

(*i*) When treated with *acetyl chloride*, the acids of this series give monacetyl derivatives ; *e.g.*,

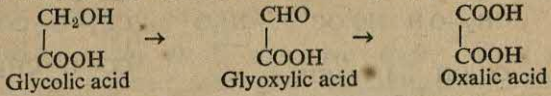
$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + CH_3COCl \longrightarrow \underset{\text{Acetyl glycolic acid}}{CH_2(OCOCH_3)COOH} + HCl$$

(*ii*) When heated with *hydriodic acid,* they are reduced to the corresponding fatty acids ; *e.g.*,

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + 2HI \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} + H_2O + I_2$$

(2) **Behaviour on Oxidation.** (*i*) A hydroxy acid containing a

primary alcohol group, on careful oxidation, gives an aldehydic acid. On further oxidation a dibasic acid results ; *e.g.*,



$$\underset{\text{Glycolic acid}}{\begin{array}{c}CH_2OH\\|\\COOH\end{array}} \rightarrow \underset{\text{Glyoxylic acid}}{\begin{array}{c}CHO\\|\\COOH\end{array}} \rightarrow \underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}}$$

(*ii*) The hydroxy acids containing a *secondary alcohol* group, on careful oxidation, give ketonic acids ; *e.g.*,

$$\underset{\text{Lactic acid}}{CH_3CH(OH)COOH} + O \rightarrow \underset{\text{Pyruvic acid}}{CH_3COCOOH} + H_2O$$

Further oxidation results in the decomposition of the ketonic acid into simpler products ; *e.g.*,

$$\underset{\text{Pyruvic acid}}{CH_3COCOOH} + O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

(3) **Reactions of the Carboxyl Group**. Hydroxy acids possess the usual properties of the carboxyl group :—

(*i*) With caustic alkalis they form salts ; *e.g.*,

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + NaOH \rightarrow \underset{\text{Sodium glycolate}}{CH_2(OH)COONa} + H_2O$$

(*ii*) When treated with alcohols in the presence of gaseous HCl, they form esters ; *e.g.*,

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl glycolate}}{CH_2(OH)COOC_2H_5} + H_2O$$

(*iii*) They form amides by the thermal decomposition of their ammonium salts ; *e.g.*,

$$\underset{\text{Ammonium glycolate}}{CH_2(OH)COONH_4} \rightarrow \underset{\text{Glycolamide}}{CH_2(OH)CONH_2} + H_2O$$

(4) **Reactions involving both the Hydroxyl and the Carboxyl Groups.** They are of two kinds :—

(*i*) When the two groups react *independently*. Thus, with phosphorus pentachloride we get a chloro-acid chloride,

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + 2PCl_5 \rightarrow \underset{\substack{\text{Chloroacetyl}\\\text{chloride}}}{CH_2ClCOCl} + 2POCl_3 + 2HCl,$$

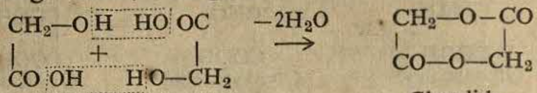
and with metallic sodium a disodium derivative :

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + 2Na \rightarrow \underset{\text{Disodium glycolate}}{CH_2(ONa)COONa} + H_2$$

(*ii*) When they both react together with elimination of water. This happens when α-, γ-, and δ-hydroxy acids are heated. β-Hydroxy acids lose water in a different way (sec. 6).

6. Action of Heat on Hydroxy Acids.—Hydroxy-acids lose water on heating, giving *different* products depending on the position of the OH group with respect to the carboxyl group.

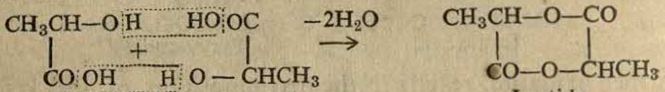
(*i*) In the case of an α-hydroxy acid, *two* molecules react in such a way that each esterifies the other (*i.e.*, the OH group of one molecule reacts with the COOH group of the other—"esterification"). The resulting **cyclic di-esters,** are called **lactides,** and have a six-membered heterocyclic ring. Thus, with glycolic acid we get glycolide,



$$CH_2{-}OH\ HO{-}OC\ (+)\ CO{-}OH\ HO{-}CH_2 \xrightarrow{-2H_2O} \begin{matrix} CH_2{-}O{-}CO \\ | \qquad\quad | \\ CO{-}O{-}CH_2 \end{matrix}$$

Olycolic acid (2 molecules) Glycolide

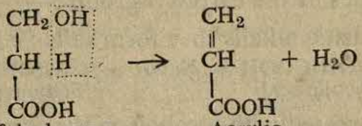
and with lactic acid we get lactide,



$$CH_3CH{-}OH\ HO{-}OC\ (+)\ CO{-}OH\ H{-}O{-}CHCH_3 \xrightarrow{-2H_2O} \begin{matrix} CH_3CH{-}O{-}CO \\ | \qquad\quad | \\ CO{-}O{-}CHCH_3 \end{matrix}$$

Lactic acid (2 molecules) Lactide

(*ii*) In the case of β-hydroxy acids one molecule of water is usually eliminated from one molecule of the acid, and an αβ-unsaturated acid is produced. Thus, β-hydroxypropionic acid yields acrylic acid :



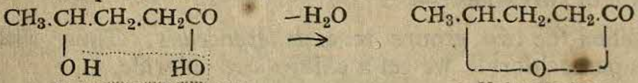
$$\begin{matrix} CH_2OH \\ | \\ CH\ H \\ | \\ COOH \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ COOH \end{matrix} + H_2O$$

β-hydroxy- propionic acid Acrylic acid

Similarly, β-hydroxybutyric acid yields crotonic acid :

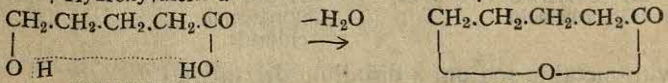
$$\underset{\text{β-hydroxybutric acid}}{CH_3CH(OH)CH_2COOH} \xrightarrow{-H_2O} \underset{\text{Crotonic acid}}{CH_3CH{=}CHCOOH}$$

(*iii*) The γ- and δ-hydroxy acids (particularly the former) show a much greater tendency to lose water than do the α- and the β-acids : So much so, that the removal of water often occurs in aqueous solution. The products are cyclic esters called **lactones** :



$$\begin{matrix} CH_3.CH.CH_2.CH_2CO \\ OH \qquad\quad HO \end{matrix} \xrightarrow{-H_2O} \begin{matrix} CH_3.CH.CH_2.CH_2.CO \\ \text{—O—} \end{matrix}$$

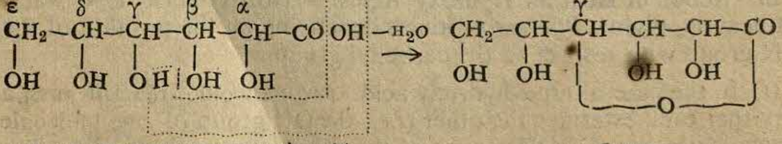
γ-Hydroxyvaleric acid γ-Valerolactone



$$\begin{matrix} CH_2.CH_2.CH_2.CH_2.CO \\ OH \qquad\qquad HO \end{matrix} \xrightarrow{-H_2O} \begin{matrix} CH_2.CH_2.CH_2.CH_2.CO \\ \text{—O—} \end{matrix}$$

δ-Hydroxyvaleric acid δ-Valerolactone

The tendency for the formation of the **5-membered γ-lactone ring** is much greater than that for the formation of the 6-membered δ-lactone ring. Thus, polyhydroxy monobasic acids of the sugar series, that have hydroxyl groups in the α-, β-, γ-, δ-, and ε- positions, produce γ-lactones only :—



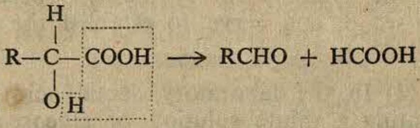
$$\begin{matrix} \varepsilon & \delta & \gamma & \beta & \alpha & \\ CH_2 & {-}CH & {-}CH & {-}CH & {-}CH & {-}CO\,OH \\ OH & OH & OH & OH & OH & \end{matrix} \xrightarrow{-H_2O} \begin{matrix} & & \gamma & & & \\ CH_2 & {-}CH & {-}CH & {-}CH & {-}CH & {-}CO \\ OH & OH & & OH & OH & \\ & & \multicolumn{4}{c}{\text{—O—}} \end{matrix}$$

α,β,γ,δ,ε-Pentahydroxycaproic acid γ-Lactone

7. Distinctive Properties of α-Hydroxy Acids :—

(1) *Lactide Formation.* (*See* sec. 6).

(2) *Decomposition by Dilute Sulphuric Acid.* When an *alpha*-hydroxy acid is warmed with dilute sulphuric acid, it decomposes into formic acid and the **next lower aldehyde** :—



$$R-\overset{H}{\underset{OH}{C}}-COOH \longrightarrow RCHO + HCOOH$$

This is a general method for the preparation of aldehydes from α-hydroxy acids.

(3) *Decomposition by Concentrated Sulphuric Acid.* When heated with concentrated sulphuric acid, *alpha*-hydroxy acids give off carbon monoxide (dehydration of formic acid, first produced).

(4) *Formation of Complex Ions* **(Ferric Chloride Test)**.—*Alpha*-hydroxy acids prevent precipitation of salts of certain heavy metals. The strongly blue coloured ion present in Fehling solution contains the complex **tartratocuprate(II) anion.** The yellow coloured solution produced by a ferric salt in the presence of an alpha-hydroxy acid (*e.g.*, tartaric or citric) is due to the formation of a ferric-complex ion having a similar structure.

A **general test** for the presence of an *alpha*-hydroxy acid is with ferric chloride solution, which produces a yellow colour. A modification of this test, called **Uffelmann's test,** is employed in biological experiments. It consists in adding a drop of ferric chloride solution to an aqueous solution of phenol (purple colour due to formation of a ferric ion complex) followed by the addition of a drop of a solution of the acid to be tested. The purple colour immediately changes to yellow due to displacement of phenol from its complex.

8. Glycolic Acid, $CH_2(OH)COOH$, (*Hydroxyacetic Acid*).—This acid occurs in unripe grapes. It may be obtained from (*i*) chloroacetic acid, (*ii*) aminoacetic acid, (*iii*) glycol, or (*iv*) formaldehyde by the general methods discussed in sec. 3. The usual method employed for the preparation of the acid consists in boiling the potassium salt of chloroacetic acid with water,

$$CH_2ClCOOK + H_2O \longrightarrow CH_2(OH)COOH + KCl,$$

evaporating the solution to dryness, and extracting the residue with acetone, which dissolves the acid, leaving behind potassium chloride.

Glycolic acid is a colourless, crystalline and hygroscopic solid, readily soluble in water, alcohol, and acetone.

9. Lactic Acid, $CH_3.CH(OH).COOH$, **α-Hydroxypropionic Acid.** This acid is present in sour milk, being produced by the *fermentation* of milk sugar contained in the milk. The fermentation is brought about by a species of bacteria known collectively as the *lactic ferment* or **lactic bacilli.** The change may be represented as follows :

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4C_3H_6O_3$$

Synthesis and Constitution. Lactic acid may be prepared synthetically : (*i*) from α-chloropropionic acid by hydrolysis, (*ii*) from acetaldehyde by the cyanohydrin synthesis. These syntheses have been discussed in sec. 3, and serve to establish the constitution of lactic acid.

Preparation. (1) In the laboratory, lactic acid can best be prepared by fermenting a dilute solution of glucose (15 per cent) by means of sour milk or old cheese, both of which contain plenty of lactic bacilli. To avoid alcoholic or butyric fermentation, the temperature must throughout be maintained at 45° to 55°C. Since the lactic bacilli are very sensitive towards free acid, the acidity of the solution must be kept low (not higher than 1 per cent) by the gradual addition of calcium carbonate or zinc carbonate. Complete neutralization is also undesirable, since it favours butyric fermentation. The sparingly soluble calcium lactate or zinc lactate, that is thus obtained, is decomposed, the former with dilute sulphuric acid and the latter with hydrogen sulphide. The insoluble calcium sulphate or zinc sulphide is filtered off, and the solution evaporated to remove water. Finally, the acid is purified by distillation *in vacuo.*

(2) On a **commercial scale,** lactic acid is obtained by the lactic fermentation of raw beet juice in vats. To keep down the acidity, lime is added periodically, and the liquid is kept stirred up by blowing in air. Calcium lactate is decomposed with dilute sulphuric acid, and the resulting liquid, after the removal of calcium sulphate, is evaporated, till the lactic acid content is about 50 per cent. The syrupy liquid thus obtained is directly put on the market.

Physical Properties. Pure lactic acid is a colourless, crystalline solid, melting at 18°. The acid, however, is rarely obtained as a solid, as it is extremely deliquescent. The usual form in which lactic acid is known is a thick syrupy liquid.

Reactions.—

(1) Lactic acid gives the usual acid reactions, and forms salts and esters.

(2) Being an *alpha*-hydroxy acid, it gives **lactide** when heated alone or with dehydrating agents (page 397).

(3) *Reaction with Sulphuric Acid.* Another important reaction of lactic acid (which is also given by other α-hydroxy acids) is with sulphuric acid. A molecule of formic acid is split off (p. 397, reaction 2). On heating with concentrated acid, the formic acid is further decomposed to give carbon monoxide.

(4) *Oxidation.* When submitted to mild oxidation, it behaves after the manner of secondary alcohols, the —CH(OH)— group

being oxidized to the —CO— group with the formation of pyruvic acid :—

$$CH_3.CH(OH).COOH + O \longrightarrow \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + H_2O$$

(5) *Holoform Reaction.* The first product of oxidation, pyruvic acid, has a *methyl group in direct attachment with a carbonyl group.* So, lactic acid (as also pyruvic acid) responds to the holoform reaction (p. 204, sec. 17). With iodine and alkali, therefore, lactic acid gives **iodoform**. This reaction differentiates lactic acid from other hydroxy acids, and is used as a **distinctive test for lactic acid.**

(6) *Other Reactions of Hydroxy Acids.* Besides the above reactions, lactic acid undergoes the usual reactions of hydroxy acids. Thus, on reduction with hydriodic acid, it gives propionic acid, on treatment with phosphorus pentachloride it yields α-chloropropionic acid, $CH_3CHClCOOH$, and then α-chloropropionyl chloride, $CH_3CHClCOCl$. Its esters undergo acetylation when treated with acetyl chloride or acetic anhydride to give the *monoacetyl derivatives.*

Tests of Lactic Acids.—

(1) Heat with concentrated sulphuric acid ; carbon monoxide is evolved that may be ignited at the mouth of the tube (blue flame).

(2) To about 5 ml. of 0·1 per cent aqueous solution of lactic acid, add 2 drops of $FeCl_3$ solution ; yellow colour discharged by dilute HCl.

(3) To a dilute solution of phenol in water, add a drop of $FeCl_3$ solution, purple colour. Now add a drop of lactic acid ; purple colour is replaced by yellow.

(4) If to a few ml. of lactic acid solution 5 ml. of concentrated sulphuric acid are added and then 2 or 3 drops of alcoholic thiophene, a cherry-red colour is developed.

(5) If to a dilute solution of lactic acid, concentrated sulphuric acid is added, and then 2 or 3 drops of a 5 per cent solution of guaiacol, a rose-red colour is developed.

Uses. (1) Lactic acid is used, along with potassium dichromate, for mordanting wool, its chief advantage being its high solubility and absence of corrosive action.

(2) It is used in tanning for the removal of lime from pelts.

(3) Lactic acid and its calcium salt are used in medicine.

10. Optical Isomerism of Lactic Acid.—*Alpha*-hydroxy-propionic acid, $CH_3CH(OH.COOH$, contains an *asymmetric carbon atom* and should, according to theory, exist in three stereoisomeric forms. All these forms are known.

dl-**Lactic acid** is obtained by the lactic fermentation of sugars or by synthesis, and is optically inactive. It is a racemic mixture consisting of equal quantities of the dextro and the levo forms.

d-**Lactic acid** or **sarcolactic acid** occurs in meat juice, hence the name (Greek, *sarkos*=flesh). It can be most readily obtained from Liebig's extract of meat. Another method consists in exposing the ordinary lactic acid to the action of *Penicilium glaucum*, which destroys the *l*-form.

l-**Lactic acid** can be obtained from the *dl* or ordinary lactic acid by resolution with strychnine (page 115), and also by the action of *Bacillus acidi levolactici* on an aqueous solution of cane-sugar.

All the three lactic acids are exactly identical in chemical behaviour. They differ, however, in their physical properties, notably the action on polarized light, the melting points and the solubility of the metallic salts. In the following table are given the more important points in which the three acids differ from one another :—

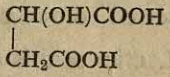
Property	*d*-Lactic acid	*l*-Lactic acid	*dl*-Lactic acid
1. Action on polarized light.	Dextro-rotatory	Levo-rotatory	Inactive
2. Melting point.	26°	26°	18°
3. Zinc salt	Crystallizes with $2H_2O$, and is readily soluble in water.	same as the *d*-lactate.	Crystallizes with $3H_2O$, and is sparingly soluble in water.

11. Hydracrylic acid, β-*Hydroxypropionic Acid,* $CH_2(OH)CH_2COOH$. This acid is prepared by heating β-chloro- or β-iodo-propionic acid with silver oxide and water, or by hydrolysing ethylene cyanohydrin.

Hydracrylic acid is a syrupy liquid, which, by elimination of water, is readily converted into acrylic acid, $CH_2=CHCOOH$.

II. DICARBOXYLIC HYDROXY-ACIDS

12. Malic Acid, *Monohydroxy-succinic acid,*



$$\begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}$$

This acid occurs in unripe apples (hence the name), grapes and the berries of the mountain-ash. It is best obtained from the last source by extraction with water, the natural product being **levo-rotatory.**

Malic acid may be synthesized in various ways, *e.g.*, from bromosuccinic acid by boiling with water and silver hydroxide, or from racemic acid[1], by reduction with hydrogen iodide. The synthetic product is inactive by external compensation and may be resolved into *d*- and *l*- forms by fractional crystallization of the cinchonine salt. The two forms can be converted into one another through the chlorosuccinic acids (see *Walden Inversion*, p. 117).

l-Malic acid forms deliquescent needles, readily soluble in water and alcohol. It melts at 100°. On further heating, it yields, according to conditions, fumaric acid or maleic anhydride.

---

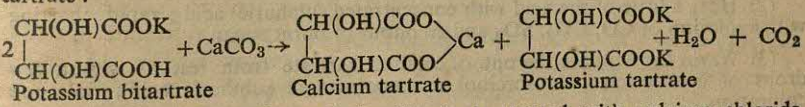
[1] Ordinarily tartaric acid on reduction with hydrogen iodide yields *d*-malic acid.

Malic acid shows the usual reactions of a hydroxy acid. Thus, it may be reduced to succinic acid by heating with hydrogen iodide and converted into monochloro-succinic acid by the action of phosphorus pentachloride. When its diethyl ester is treated with acetyl chloride an acetate of the formula, $C_2H_5OOC.CH(O.CO.CH_3)CH_2.COOC_2H_5$, is formed.

12. *d*-Tartaric Acid, $\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}$, *Dihydroxy-succinic Acid*

Dihydroxy-butane diacid.—As already mentioned (chap. 7, sec. 6, p. 110) this acid occurs in four different forms. The ordinary acid is dextrorotatory and, in the form of its acid potassium salt, occurs in grapes and other fruits. The crude salt, known as **argol** or *tartar*, is a by-product of the alcohol industry. It is recrystallized from hot water, and the pure product, called **cream of tartar**, thus obtained, is employed for the commercial preparation of tartaric acid :

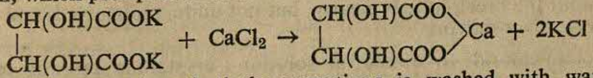
Cream of tartar is dissolved in water and the solution is neutralized with calcium carbonate. Half of the tartaric acid is thus precipitated as insoluble calcium tartarate while the other half remains in solution as normal potassium tartrate :



$$2\begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOH\end{array} + CaCO_3 \rightarrow \begin{array}{l}CH(OH)COO\\ |\\ CH(OH)COO\end{array}\!\!>Ca + \begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOK\end{array} + H_2O + CO_2$$

Potassium bitartrate — Calcium tartrate — Potassium tartrate

The precipitate is filtered off, and the filtrate is treated with calcium chloride solution, which precipitates the remaining half of the acid as calcium tartrate :



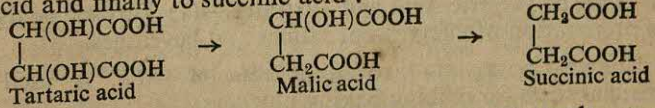
$$\begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOK\end{array} + CaCl_2 \rightarrow \begin{array}{l}CH(OH)COO\\ |\\ CH(OH)COO\end{array}\!\!>Ca + 2KCl$$

The calcium tartrate from both the operations is washed with water, and then decomposed with calculated quantity of dilute sulphuric acid. The precipitated calcium sulphate is filtered off, and the solution is evaporated to obtain crystals of tartaric acid.

Physical Properties. *d*-Tartaric acid crystallizes in monoclinic, anhydrous prisms. It melts at about 167°, the melting point being not sharp because of decomposition. It is very readily soluble in water, less so in alcohol, and insoluble in ether. When heated with water under pressure, it yields racemic acid, *i.e.*, *dl*-tartaric acid.

Chemical Properties. (1) Tartaric acid, $H_2(C_4H_4O_6)$, being a dibasic acid forms normal as well as acid salts and esters ; *e.g.*, $KH(C_4H_4O_6)$ and $K_2(C_4H_4O_6)$.

(2) On being heated with hydrochloric acid, it gets reduced to malic acid and finally to succinic acid :

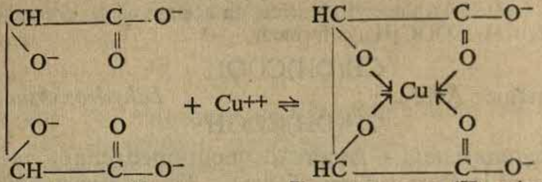


$$\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array} \rightarrow \begin{array}{l}CH(OH)COOH\\ |\\ CH_2COOH\end{array} \rightarrow \begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$$

Tartaric acid — Malic acid — Succinic acid

(3) Like glycerol and other polyhydroxy compounds, tartaric acid has the property of preventing the precipitation of the hydroxides of the heavy metals. Thus, Fehling's solution contains the complex **cupri-tartrato anion** produced by the co-ordination of the

cupric ion (co-ordination number 4) with the tetravalent tartrate anion :—



Tartrato anion
(tartravalent negative)

Tartratocuprate (II) anion
(divalent negative)

The bright blue solution that results contains the sodium and potassium salts of the complex.

Expt. 1. Dissolve some Rochelle salt in a solution of copper sulphate and add sodium hydroxide. No precipitate is formed, and the solution acquires a deep blue colour.

Expt. 2. Tests of Tartaric Acid. (1) Heat a little of the acid in a dry test tube; immediate charring with the evolution of an odour of burnt sugar.

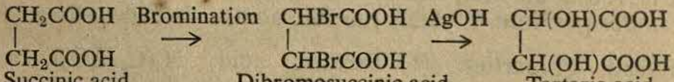
(2) Heat a little of the acid with concentrated sulphuric acid ; rapid charring with evolution of CO, CO_2, SO_2 and an odour of burnt sugar.

(3) Warm the acid (or the ppt. of calcium tartrate from test 5) with a few drops of a solution of resorcinol in concentrated sulphuric acid ; violet-red coloration.

(4) Add silver nitrate to a *neutral* solution ; white ppt. Add dilute ammonia, drop by drop, until the precipitate is nearly, but not quite, redissolved, and gently heat the mixture ; silver mirror.

(5) Add calcium chloride to a neutral solution ; crystalline ppt. of calcium tartrate, insoluble in acetic acid.

Synthesis and Constitution. Optically inactive tartaric acid, which consists of a mixture of racemic acid and mesotartaric acid, can be obtained synthetically from succinic acid. The latter is first converted into dibromosuccinic acid by treatment with bromine and red phosphorus. The dibromo-derivative, when heated with water and silver hydroxide, yields tartaric acid :



$$\begin{array}{c}CH_2COOH\\ |\\ CH_2COOH\end{array} \xrightarrow{\text{Bromination}} \begin{array}{c}CHBrCOOH\\ |\\ CHBrCOOH\end{array} \xrightarrow{\text{AgOH}} \begin{array}{c}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}$$

Succinic acid Dibromosuccinic acid Tartaric acid

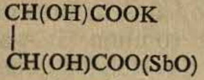
The above synthesis of tartaric acid and its conversion into succinic acid by reduction prove that the acid is **dihydroxy-succinic acid.**

13. Uses of Tartaric Acid and Tartrates.—(1) Tartaric acid is used in the preparation of effervescent salines and beverages.

(2) The acid potassium tartrate, or **cream of tartar**, is used on a commercial scale for making baking powders.

(3) **Rochelle salt** or potassium sodium tartrate (got by neutralizing potassium hydrogen tartrate with sodium carbonate) is used in the preparation of **Fehling's solution.** This contains copper sulphate, Rochelle salt and sodium hydroxide, and is employed in the detection

and estimation of glucose and certain other oxidizable organic substances.



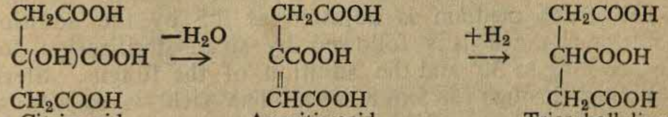
(4) **Tartar emetic**, $\begin{array}{l} CH(OH)COOK \\ | \\ CH(OH)COO(SbO) \end{array}$, or potassium antimonyl tartrate, is used as an emetic and as a mordant in dyeing and calico-printing.

14. Optical Isomerism of Tartaric Acid.—The stereoisomerism of tartaric acids has already been discussed (chap. 7, sec. 6, p. 110) *dl*-Tartaric acid or **racemic acid** occurs, along with *d*-tartaric acid, in grape-juice and can be isolated from the argol mother liquors. It may be readily synthesized from dibromosuccinic acid or by the oxidation of fumaric acid. ***l*-Tartaric acid** is obtained by the resolution of racemic acid. **Maso-tartaric acid**, the internally compensated form, is obtained by the oxidation of maleic acid and by heating *d*-tartaric acid with water at 165° in a sealed tube.

The physical properties of all the four tartaric acids and their sodium-ammonium and potassium-hydrogen salts are tabulated on page 111. Their respective space formulae are given on page 112. All of them, of course, show identical chemical properties.

III. TRICARBOXYLIC HYDROXY-ACIDS

15. Tricarboxylic Acids.—The tricarboxylic acids contain three carboxyl groups linked to three different carbon atoms. The three chief tricarboxylic acids and their interconnection is shown below :—



Citric acid
(β-Hydroxy-propane-tricarboxylic acid)

Aconitic acid
(Propene-tricarboxylic acid)

Tricarballylic acid
(Propane-tricarboxylic acid)

16. Citric Acid, β-*Hydroxy-propanetricayboxylic Acid*, β-*Hydroxy-tricarballylic Acid.*—This hydroxy-acid is the most important of the tricarboxylic acids.

Occurrence. Citric acid is one of the most widely distributed acids in fruits with a sour taste, especially lemons, *galgals* and unripe oranges. It is also found in certain berries, beet juice and wine.

Manufacture of Citric Acid. Citric acid is manufactured from two different sources, (*i*) citrus fruit and (*ii*) molasses. Before 1923, Italy produced about 90 per cent of the world supply by extraction from citrus fruit. In that year microbiological production from molasses was started in U.S.A. The development has been very rapid indeed, and at present over 93 per cent of world's production of citric acid comes from molasses.

(1) **From Lemons.** In Italy, citric acid is prepared from the juice of cull lemons through its insoluble calcium salt. The juice (that

contains about 6 to 7 per cent of citric acid) is first boiled to coagulate albuminous matter, which is filtered off. The filtrate is neutralized with chalk and boiled. The precipitate of calcium citrate, which separates from the *hot* solution, is washed with hot water, and then decomposed with the calculated quantity of sulphuric acid. Calcium sulphate is filtered off, and the solution is concentrated to obtain crystals of citric acid :

$$\underset{\text{Citric acid}}{2H_3(C_6H_5O_7)} + 3CaCO_3 \rightarrow \underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + 3H_2O + 3CO_2$$

$$Ca_3(C_6H_5O_7)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3(C_6H_5O_7)$$

(2) **From Molasses.** Citric acid is now chiefly prepared by **aerobic fermentation** of waste sugar (molasses) with a special strain of the fungus **Aspergillus niger.** The over-all reaction is represented by the equation :

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + 3O_2 \longrightarrow \underset{\text{Citric acid}}{2C_6H_8O_7} + 3H_2O$$

The fermentation involves oxidation, and changes a straight-chain into a branched chain :

The medium to be subjected to fermentation is carefully prepared from :—

(*a*) decationized molasses,

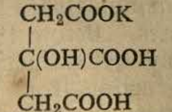
(*b*) decationized water,

(*c*) the following nutrients : ammonium carbonate, primary potassium phosphate and magnesium sulphate.[1]

The *p*H of the medium is adjusted at 2·5 by the addition of hydrochloric acid This is followed by steam-sterilization for 20 minutes, cooling to 30° and the addition of the fungus. Sterilized air is bubbled through for 5 to 8 days. The yield is approximately 80 per cent on the basis of the above equation.

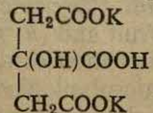
Physical Properties. Citric acid is readily soluble in water and in alcohol, but is only sparingly soluble in ether. From the aqueous solution, the acid crystallizes in large rhombic prisms, which contain 1 molecule of water and melt at 100°C. The water of crystallization is not lost until the temperature has gone up to 130°C. The anhydrous acid melts at 153°.

Reactions. (1) *Formation of Salts and Esters.* Citric acid is tribasic, and forms *three* series of salts, *e.g.*,



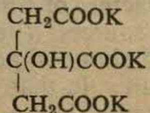
$$\begin{array}{c} CH_2COOK \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array}$$

Mono-potassium citrate



$$\begin{array}{c} CH_2COOK \\ | \\ C(OH)COOH \\ | \\ CH_2COOK \end{array}$$

Di-potassium citrate



$$\begin{array}{c} CH_2COOK \\ | \\ C(OH)COOK \\ | \\ CH_2COOK \end{array}$$

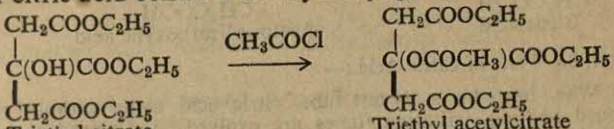
Tri-potassium citrate

---

[1] Addition of 500 parts per million of morpholine is reported to increase the efficiency of the process to a considerable extent.

Similarly, with ethyl alcohol, citric acid forms mono-, di-, and tri-ethyl citrates.

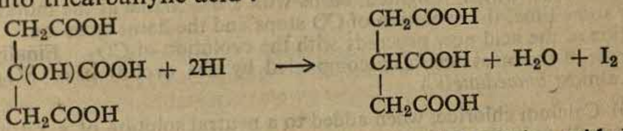
(2) *Acetylation.* The normal ethyl ester, when treated with acetyl chloride, gives a *monoacetyl* derivative, thus showing that the molecule of citric acid contains one hydroxyl group :



$$\begin{array}{l}CH_2COOC_2H_5\\ |\\ C(OH)COOC_2H_5\\ |\\ CH_2COOC_2H_5\end{array}\xrightarrow{CH_3COCl}\begin{array}{l}CH_2COOC_2H_5\\ |\\ C(OCOCH_3)COOC_2H_5\\ |\\ CH_2COOC_2H_5\end{array}$$

Triethyl citrate — Triethyl acetylcitrate

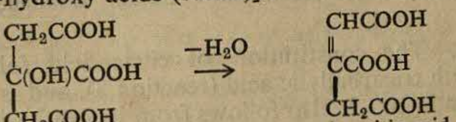
(3) *Reduction.* When reduced with hydriodic acid, citric acid is converted into tricarballylic acid :



$$\begin{array}{l}CH_2COOH\\ |\\ C(OH)COOH\\ |\\ CH_2COOH\end{array} + 2HI \longrightarrow \begin{array}{l}CH_2COOH\\ |\\ CHCOOH\\ |\\ CH_2COOH\end{array} + H_2O + I_2$$

(4) *Complex Anion Formation.* Like tartaric acid, citric acid has the power of preventing the precipitation of the hydroxides of certain heavy metals because of complex-ion formation.

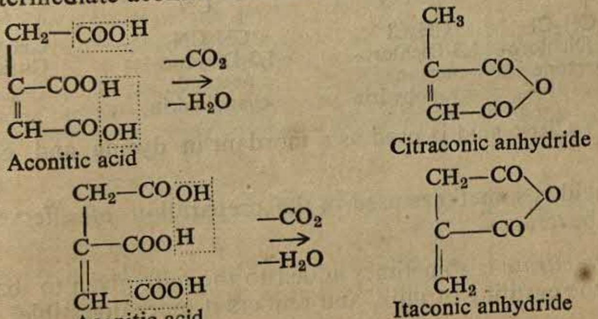
(5) *Action of Heat.* (*i*) When heated at 175°, citric acid loses a molecule of water, and is converted into **aconitic acid** [compare the behaviour of β-hydroxy acids (sec. 6)] :



$$\begin{array}{l}CH_2COOH\\ |\\ C(OH)COOH\\ |\\ CH_2COOH\end{array}\xrightarrow{-H_2O}\begin{array}{l}CHCOOH\\ \|\\ CCOOH\\ |\\ CH_2COOH\end{array}$$

Citric acid — Aconitic acid

(*ii*) Rapid distillation of citric acid results in the production of **anhydrides of itaconic and citraconic acids** by the elimination, in each case, of a molecule of carbon dioxide and a molecule of water from the intermediate aconitic acid in two different ways :—



$$\begin{array}{l}CH_2—COOH\\ |\\ C—COOH\\ \|\\ CH—COOH\end{array}\xrightarrow[-H_2O]{-CO_2}\begin{array}{l}CH_3\\ |\\ C—CO\\ \| \qquad\quad \rangle O\\ CH—CO\end{array}$$

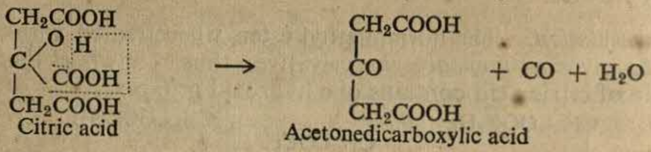
Aconitic acid — Citraconic anhydride

$$\begin{array}{l}CH_2—COOH\\ |\\ C—COOH\\ \|\\ CH—COOH\end{array}\xrightarrow[-H_2O]{-CO_2}\begin{array}{l}CH_2—CO\\ | \qquad\quad \rangle O\\ C—CO\\ \|\\ CH_2\end{array}$$

Aconitic acid — Itaconic anhydride

(6) *Decomposition by Sulphuric Acid.* A very important decomposition of citric acid is the one that occurs on heating with concentrated sulphuric acid. Like other α-hydroxy-acids and α-keto acids,

a molecule each of carbon monoxide and water (or formic acid) is lost with the production of **acetonedicarboxylic acid** :—



Expt. 3. Tests of Citric Acid :—

(1) When heated in a dry test tube, citric acid melts without charring. On continued heating, irritating fumes are evolved, and a *gradual* charring occurs (contrast tartaric acid).

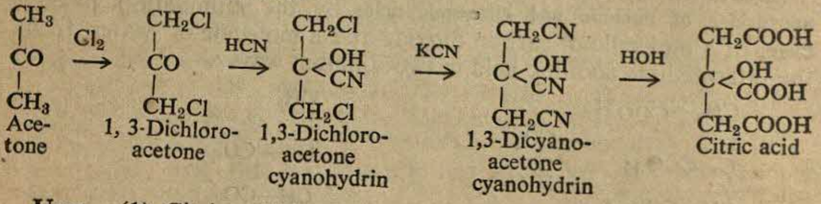
(2) When citric acid or a citrate is warmed with concentrated sulphuric acid, CO is evolved, which, if lighted, burns with a blue flame at the mouth of the tube. After some time, the evolution of CO stops and the flame goes out. The decomposition of the acid now proceeds with the evolution of CO_2. Finally, a *gradual* charring of the mass occurs, accompanied by the evolution of SO_2. (Tartrates char almost *immediately*.)

(3) Calcium chloride, when added to a neutral solution of a citrate, produces no precipitate in the cold. On *boiling* the liquid for some time, a white crystalline precipitate of calcium citrate is formed, as the salt is less soluble in hot than in cold water. This behaviour, together with the fact that the precipitate is insoluble in KOH distinguishes citric acid from tartaric acid.

(4) When silver nitrate is added to a neutral solution of a citrate, a white precipitate of silver citrate is produced. If the precipitate be just dissolved in dilute ammonia, and the mixture heated by placing the tube in hot water, no silver mirror is produced (distinction from tartrates). Continued boiling causes slight reduction.

Constitution. The constitution of citric acid follows from its relationship with tricarballylic acid (reaction 3), and is supported by reactions (1) and (2). It also follows from its synthesis from acetone given below.

Synthesis from Acetone:—



Uses. (1) Citric acid is used as a mordant in dyeing and calico-printing.

(2) The acid is sometimes used in the preparation of effervescent salines and beverages.

(3) *Sodium citrate* is sometimes added to the milk given to babies. It prevents the curdling of milk, and renders it more digestible.

(4) *Ferric ammonium citrate*, together with potassium ferricyanide is employed in making blue-prints. This use is based on the reduction of the ferric ion by the citrate ion in the presence of light.

QUESTIONS

(1) Describe the general methods of preparation of hydroxy acids and their general reactions. Give the distinction between α-, β-, and γ-hydroxy acids.

(2) Describe the characteristic behaviour of α-, β-, and γ-hydroxy-acids. (*Agra, B.Sc.. 1942*)

3. How do you say that lactic acid is (*a*) an α-hydroxy acid, and (*b*) a derivative of propionic acid ? How does it differ from its isomer ? (*Delhi, B.Sc., 1953*)

4. How is lactic acid synthesized ? Describe its properties. Give an account of stereoisomerism of lactic acid. (*Mysore, B.Sc., 1953*)

5. What is ordinary lactic acid and how is it prepared commercially ? What is the action of (*a*) heat, (*b*) potassium permanganate, (*c*) dilute sulphuric acid, and (*d*) iodine and alkali on it ? Discuss the stereoisomerism of lactic acids. (*Patna, B.Sc., 1954*)

6. How is tartaric acid obtained ? How many modifications of tartaric acid are known and how would you account for their occurrence ? Give an account of the characteristic reactions of tartaric acid by which you can distinguish it from oxalic acid. (*Andhra, B.Sc., 1954*)

7. On analysis, a monobasic organic acid *A* was found to contain C=40·0%, H=6·66% and O=53·34%. 0·985 g. of its silver salt gave on ignition 0·54 g. of the metal. On treatment with HI, the acid gave another acid *B*. The original acid *A* on heating lost water and left a third acid *C*. What is the constitutional formula for each of the acids A, B and C ? Explain the reactions. (*Nagpur, B.Sc., 1952*)

Ans. (*A*) β-Hydroxy propionic acid, $CH_2(OH).CH_2COOH$ (*B*) Propionic acid, CH_3CH_2COOH (*C*) Acrylic acid, $CH_2=CHCOOH$.

8. How is lactic acid synthesised ? State its properties and uses. Give a brief account of the stereoisomerism of lactic acid. (*Andhra, B.Sc., 1957*)

9. How can pure tartaric acid be obtained from its sodium salt, containing soluble impurities ? How does tartaric acid react towards (*i*) hydriodic acid and (*ii*) hydrogen peroxide ? Write a note about its optical activity. (*Rajasthan, B.Sc., 1957*)

10. Give an account of the manufacture and reactions of citric acid. Establish its structure. (*Delhi, B.Sc., 1958*)

11. Discuss the constitution of Tartaric Acid. (*Lucknow, B.Sc., Prev., 1962*)

12. How is the molecular weight of an organic acid determined ?

0·1072 gm. of a dibasic acid, *A*, gave 0·1408 gm. of carbon dioxide and 0·3432 gm. of water. 0·3480 gm. of the silver salt of *A* left 0·2160 gm. of silver on ignition. On rapid distillation, *A* was converted into the anhydride, *B*, of the acid, which gave carbon=49·0 and hydrogen=2·04 per cent. The acid derived from *B* absorbed two atoms of hydrogen on catalytic reduction. What is the substance *A* ? (*Punjab, B.Sc., 1939*)

Ans. *A*=malic acid ; *B*=maleic anhydride.

13. Analysis of an organic dibasic acid gave the following results :—

(*a*) 0·166 gm. on combustion gave 0·352 gm. CO_2 and 0·054 gm. H_2O.

(*b*) 0·190 gm. of its silver salt gave 0·108 gm. silver.

(*c*) The acid when heated eliminated a molecule of water yielding acid anhydride.

Determine the molecular formula of the acid and give a method for its preparation from a simple source. (*Lucknow, B.Sc., 1951*)

14. Discuss the constitution of Lactic Acid. (*Lucknow, B Sc., Prev., 1962*)

15. What methods are available for the preparation of hydroxy acids ? How would you distinguish between α, β and γ-hydroxy acids ?

Why is lactic acid given the structure $CH_3.CHOH.COOH$?

(*Rangoon, B.Sc., 1958*)

16. Describe the preparation of tartaric acid and discuss briefly the isomerism exhibited by this acid. (*Venkateswara, B.Sc., 1960*)

17. How is citric acid manufactured ? Discuss the constitution of citric acid.

(*Gorakhpur, B.Sc., 1961*)

18. What methods are available for the preparation of aliphatic hydroxy acids ? Give a general account of the properties of the different kinds of hydroxy acids.

(*Venkateswara, B.Sc., 1961*)

19. How are the following acids synthesised ?—

(*a*) Citric acid ; (*b*) Tartaric acid ; (*c*) Oxalic acid. How do you distinguish them from one another ? (*Andhra, B.Sc., 1961*)

20. How is citric acid manufactured ?

What happens when (*i*) Citric acid is heated ; (*ii*) ethyl citrate is reacted with acetyl chloride ; (*iii*) Citric acid is digested with conc. sulphuric acid and (*iv*) Citric acid is oxidised with permanganate. (*Punjab, B.Sc., 1961*)

21. How is lactic acid prepared ? Explain fully the optical isomerism of the lactic acids. Why is the lactic acid optically inactive when prepared synthetically ?

(*Saugar, B.Sc., 1962*)

22. How do you arrive at the structure of citric acid ? Starting from acetone, how would you synthesise it ? (*Bihar, B Sc., 1962*)

23. What is the natural source of citric acid ? Describe its method of preparation and show how its constitution has been established. Is it optically active ? If not, why ? (*Utkal, B.Sc., 1962*)

24. Synthesis of an organic compound is absolutely essential in order to prove its structure satisfactorily. Indicate the applicability of this statement in the case of citric acid.

(*Patna, B.Sc., 1959*)

25. How is citric acid prepared from natural sources ? Discuss its structure.

(*Calcutta, B.Sc., 1959*)

26. How would you prepare a sample of pure tartaric acid from grapes ? Discuss its stereoisomerism. (*Punjab, Pakistan, B.Sc., 1954*)

27. How will you distinguish between *alpha*, *beta* and *gamma* hydroxy-aliphatic acids ? (*Bombay, B.Sc., Chemistry, Sub., 1962*)

28. Give reactions to show that lactic acid (*a*) is a hydroxy acid, (*b*) has the hydroxy group in the α-position and (*c*) is a derivative of propionic acid.

(*Agra, B.Sc., 1959*)

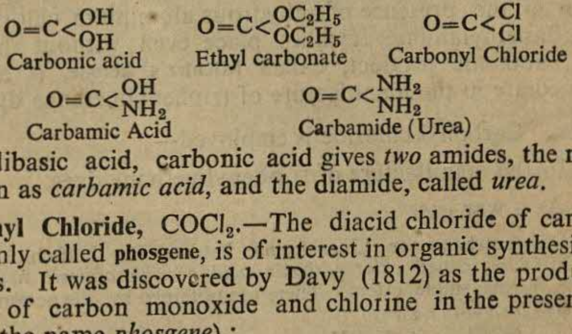
29. Describe the synthesis of citric acid. (*Agra, B.Sc., 1958*)

CHAPTER TWENTY-FIVE

CARBONIC ACID AND ITS DERIVATIVES

1. **Carbonic Acid,** $HO{-}C\begin{array}{l}\diagup O\\ \diagdown OH\end{array}$, is a monohydroxy monocarboxylic acid, and may be regarded as **Hydroxy formic acid.** It is, therefore, the first member of the glycollic acid series. It, however, differs from the other members of the series in being *dibasic* (but not a dicarboxylic) acid.

The anhydride of carbonic acid, *i.e., carbon dioxide,* and its metallic salts, known as *carbonates* and *bicarbonates,* are described in text-books of inorganic chemistry. Some of the derivatives of carbonic acid that are of interest to organic chemist are described in this chapter. The following scheme will serve to illustrate the relationship between the acid and its more important derivatives :



$$O{=}C{<}\begin{smallmatrix}OH\\OH\end{smallmatrix} \qquad O{=}C{<}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} \qquad O{=}C{<}\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$$

Carbonic acid — Ethyl carbonate — Carbonyl Chloride

$$O{=}C{<}\begin{smallmatrix}OH\\NH_2\end{smallmatrix} \qquad O{=}C{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$$

Carbamic Acid — Carbamide (Urea)

Being a dibasic acid, carbonic acid gives *two* amides, the monoamide, known as *carbamic acid,* and the diamide, called *urea.*

2. **Carbonyl Chloride,** $COCl_2$.—The diacid chloride of carbonic acid, commonly called **phosgene,** is of interest in organic synthesis and as a war gas. It was discovered by Davy (1812) as the product of combination of carbon monoxide and chlorine in the presence of light (hence, the name *phosgene*) :

$$CO + Cl_2 \rightleftharpoons COCl_2$$

The reaction is reversible, and the gas is completely decomposed into CO and Cl_2 at about 800°.

Manufacture. Phosgene is now manufactured from carbon monoxide and chlorine with activated charcoal as catalyst. The reaction is carried out at 200°.

Properties. Phosgene is a colourless, highly toxic gas. It injures the lungs in the same way as chlorine, but is said to be ten times stronger.

Reactions. The reactions of phosgene are those of an acid chloride :—

(1) *Hydrolysis.* It is gradually decomposed by water, giving carbonic acid and hydrochloric acid,

$$COCl_2 + 2HOH \longrightarrow \underset{\substack{\text{Carbonic acid} \\ \text{(unstable)}}}{CO(OH)_2} + 2HCl$$

$$\rightleftharpoons$$

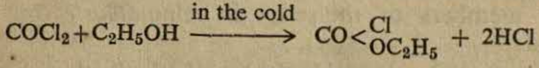
$$H_2O + CO_2$$

The **poisonous action** of phosgene is attributed to its hydrolysis in the tissues to give hydrochloric acid, which is a direct poison for the cells.

(2) *Ammonolysis.* With ammonia, phosgene gives urea (the diamide of carbonic acid),

$$COCl_2 + 2NH_3 \longrightarrow \underset{\text{Urea}}{CO(NH_2)_2} + 2HCl$$

(3) *Reaction with Alcohols.* This occurs in two stages ; *e.g.*,



$$COCl_2 + C_2H_5OH \xrightarrow{\text{in the cold}} CO{<}{\substack{Cl \\ OC_2H_5}} + 2HCl$$

Ethyl chlorocarbonate

$$COCl(OC_2H_5) + C_2H_5OH \xrightarrow{\text{on heating}} \underset{\text{Ethyl carbonate}}{CO(OC_2H_5)_2} + HCl$$

(4) *Friedel-Crafts Reaction.* Phosgene reacts with aromatic compounds to give acid chlorides and ketones. The reaction generally occurs in the presence of anhydrous aluminium chloride (catalyst). With dimethylaniline it takes place even without the addition of $AlCl_3$, and the product, called **Michler's ketone**, is an important intermediate in the manufacture of triphenylmethane dyes.

Uses. Carbonyl chloride is employed—

(1) In the manufacture of triphenylmethane dyes.

(2) As a war gas.

3. Chlorocarbonic or Chloroformic Esters.—The half-chloride of carbonic acid, ClCOOH, called *chlorocarbonic acid* or *chloroformic acid*, though itself unstable, forms stable esters. These are obtained by the action of phosgene on alcohols *in the cold* ; *e.g.*,

$$COCl_2 + C_2H_5OH \rightarrow \underset{\text{Ethyl chlorocarbonate}}{ClCOOC_2H_5} + HCl$$

Chlorocarbonic esters are volatile liquids with a suffocating odour. They are esters as well as acid chlorides. Like the latter, they react with alcohols, phenols, amines, etc., replacing the reactive hydrogen by the esterified carboxyl group ; *e.g.*,

$$C_2H_5O|\underline{H + Cl}|COOR \rightarrow C_2H_5OCOOR + HCl$$

$$C_2H_5NH\underline{H + Cl}|COOR \rightarrow C_2H_5NHCOOR + HCl$$

The products in the first case are neutral esters of carbonic acid, and in the second case esters of carbamic acid (which are known as **urethans**).

4. Carbonic Esters, $CO(OR)_2$.—The diesters of carbonic acid, obtained by heating chlorocarbonic esters with alcohols, are neutral liquids with an ethereal odour. They are employed as **alkylating agents** in certain reactions ; *e.g.*,

$$Na(CH_3)C{<}{\substack{COOC_2H_5 \\ COOC_2H_5}} + CO(OCH_3)_2 \rightarrow (CH_3)_2C{<}{\substack{COOC_2H_5 \\ COOC_2H_5}} + CH_3NaCO_3$$

Sodio-methylmalonic ester　　Methyl carbonate　　Dimethylmalonic ester

5. **Urethans.**—The esters of carbamic acid, H_2NCOOH, known as *urethans*, may be obtained from chlorocarbonic esters by the action of ammonia,

$$NH_2H + ClCOOC_2H_5 \rightarrow NH_2COOC_2H_5 + HCl$$

or by heating urea with alcohols,

$$NH_2CONH_2 + HOC_2H_5 \rightarrow NH_2COOC_2H_5 + NH_3.$$

Urethans are colourless, crystalline compounds that distil without decomposition. They are hydrolysed by alkalis to give ammonia, carbon dioxide and alcohols.

The ethyl ester, commonly called **urethan**, melts at 49° and boils at 184°. It is often employed as a narcotic in experiments with smaller animals. Other urethans find use in medicine as sedatives, hypnotics and antipyretics.

6. **Urea,** *Carbamide*, H_2NCONH_2.—The name *urea* is derived from the occurrence of the compound in mammalian urine, being formed in the body as the final metabolic product of proteins. A fully grown man excretes about 30 grams of urea per day.

Preparation :—

(1) **From urine.** Urea may be obtained from urine by evaporating the liquid to a small bulk, and adding concentrated nitric acid, when **urea nitrate,** $H_2NCONH_2.HNO_3$, separates out as a crystalline precipitate. This, on account of the impurities present, has a yellow colour, which is removed by dissolving the precipitate in water and adding potassium permanganate. The solution is then treated with barium carbonate to set free urea :

$$2NH_2CONH_2.HNO_3+BaCO_3 \rightarrow 2NH_2CONH_2+Ba(NO_3)_2+H_2O+CO_2$$

The liquid is evaporated to dryness, and the urea is extracted from the residue by means of alcohol, in which barium nitrate is insoluble.

(2) **From ammonium cyanate.** Urea may be prepared in the laboratory by **Wohler's method,** *viz*, by evaporating an aqueous solution of ammonium sulphate and potassium cyanate. The ammonium cyanate, formed by the double decomposition between the two salts, gets converted into urea by intramolecular rearrangement :

$$2KOCN + (NH_4)_2SO_4 \rightleftharpoons 2NH_4OCN + K_2SO_4$$

$$NH_4OCN \rightleftharpoons NH_2CONH_2$$

The potassium sulphate crystallizes out on cooling, and is filtered off. The filtrate is evaporated to dryness, and the urea is extracted from the residue with alcohol.

(3) **From carbonyl chloride.** Urea may also be prepared in the laboratory by the action of ammonia on carbonyl chloride (phosgene) :

$$\underset{\text{Carbonyl chloride}}{COCl_2} + 4NH_3 \rightarrow \underset{\text{Urea}}{CO(NH_2)_2} + 2NH_4Cl$$

Manufacture :—

(1) **From carbon dioxide and ammonia.** Urea is manufactured on a large scale by the interaction of liquid ammonia and liquid carbon dioxide under high pressure, when ammonium carbamate is pro-

duced. This when heated at 200° under pressure loses water to give urea :—

$$\underset{\text{}}{CO_2} + 2NH_3 \rightleftharpoons \underset{\text{Ammonium carbamate}}{NH_2COONH_4} \rightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

(2) **From cyanamide.** Another method for the large-scale production of urea is by the partial hydrolysis of cyanamide,

$$\underset{\text{Cyanamide}}{H_2N\text{—}C{\equiv}N} + H_2O \rightarrow \underset{\text{Urea}}{H_2N\text{—}CO\text{—}NH_2}$$

Physical Properties. Urea crystallizes from water in long colourless prisms. It melts at 132°, and is soluble in water and alcohol.

Reactions. Urea possesses the general chemical behaviour of an amide. Its more important reactions are :—

(1) *Basic Nature.* Urea is a weak monoacid base, and forms crystalline salts with strong acids. The two most characteristic salts of urea are **urea nitrate,** $H_2NCONH_2.HNO_3$, or $[H_2NCONH_3]NO_3$, and **urea oxalate,** $[H_2NCONH_2]_2.H_2C_2O_4$, or $[H_2NCONH_3]_2C_2O_4$.

These are obtained as crystalline precipitates by adding concentrated nitric acid or oxalic acid to a saturated solution of urea. When examined under the microscope, the nitrate is seen to consist of rhombic, six-sided plates, which are often imbricated (like tiles), while the oxalate forms short, rhombic prisms.

(2) *Hydrolysis.* When heated with a dilute mineral acid, or an alkali, urea is hydrolysed to give ammonia and carbonic acid :

$$NH_2CONH_2 + 2HOH \rightarrow 2NH_3 + H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

The hydrolytic decomposition of urea with **urease,** an enzyme present in soya beans, is utilized in the **estimation of urea.**

(3) *Action of Nitrous Acid.* Urea is decomposed by nitrous acid with the evolution of carbon dioxide and nitrogen :

$$NH_2CONH_2 + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O$$

The reaction, however, is *not* quantitative.

(4) *Action of Sodium Hypobromite.* When treated with an alkaline solution of sodium hypobromite, urea is decomposed with evolution of nitrogen, the carbon dioxide produced in the reaction being retained by the alkali :

$$NH_2CONH_2 + 3NaOBr \rightarrow N_2 + CO_2 + 2H_2O + 3NaBr$$
$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

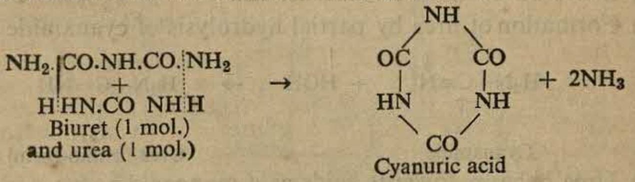
This reaction is also utilized for the **estimation of urea.**

(5) *Action of Heat.* When urea is heated in a dry tube, it first melts, and then begins to evolve ammonia. Finally, the mass solidifies, and a ring of sublimed cyanuric acid may be formed on the upper cool portion of the tube.

The white residue consists mainly of **biuret**, which is produced by the condensation of two molecules of urea with the elimination of a molecule of ammonia :

$$\underset{\text{Urea (2 molecules)}}{NH_2.CO.\boxed{NH_2 + H}\,NH.CO.NH_2} \rightarrow \underset{\text{Biuret}}{NH_2.CO.NH.CO.NH_2} + NH_3$$

It also contains a small proportion of **cyanuric acid**, formed by the further condensation of biuret with unchanged urea :



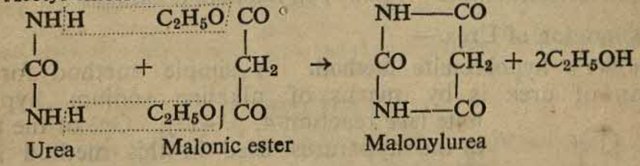
On shaking the solid in the tube with water, the biuret dissolves. If the solution be poured off and tested with a few drops of sodium hydroxide and a drop of the dilute copper sulphate solution, a pink coloration is developed **(biuret reaction).**

If the residue in the tube be dissolved in dilute ammonia, and a portion of the solution treated with barium nitrate, a white precipitate of **barium cyanurate**, is formed. The other part of the ammonium cyanurate solution, if treated with copper sulphate, gives a violet precipitate of **copper cyanurate.**

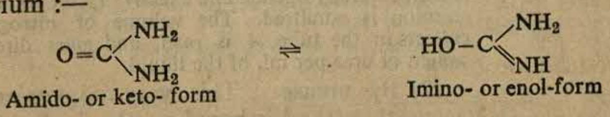
(6) *Reaction with Alcohols.* Urea when heated with alcohols. gives *urethans* (Sec. 5).

(7) *Reaction with Acid Chlorides and Esters.* Urea reacts with acid chlorides and esters in the same way as ammonia, giving **ureides :**

$$\underset{\text{Acetyl chloride}}{CH_3CO\,\boxed{Cl + H}\,NHCONH_2} \rightarrow \underset{\text{Acetylurea}}{CH_3CONHCONH_2} + HCl$$



7. Constitution of Urea.—The evidence as regards the constitution of urea is of a conflicting nature. Certain facts agree with the **amide formula**, while others point to the **imino formula**. Hence, urea is regarded as a tautomeric substance consisting of the two forms in equilibrium :—



(*a*) **Evidence in favour of the amide formula :—**

(1) Formation of urea by the action of ammonia on carbonyl chloride or ethyl carbonate.

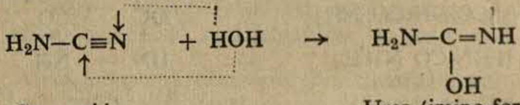
(2) When urea is hydrolysed (with a caustic alkali), *two* molecules of ammonia are set free.

(3) The reaction with nitrous acid indicates the existence of *two* NH_2 groups in the molecule.

(4) X-ray and crystallographic evidence also indicates the amide structure.

(*b*) **Evidence in favour of the imino formula :—**

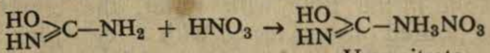
(1) Formation of urea by partial hydrolysis of cyanamide :—



$$H_2N{-}C{\equiv}N + HOH \rightarrow H_2N{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}NH$$

Cyanamide Urea (imino-form)

(2) Urea behaves towards acids as a monoacid base : *e.g.*,



$$\begin{matrix}HO\\HN\end{matrix}{\geqslant}C{-}NH_2 + HNO_3 \rightarrow \begin{matrix}HO\\HN\end{matrix}{\geqslant}C{-}NH_3NO_3$$

Urea nitrate

Amides do not behave this way.

(3) Raman spectrum of urea indicates the presence of $>C{=}N{-}$ grouping.

8. Tests of Urea.—(*i*) *Biuret reaction.* Heat a few crystals of urea in a dry test-tube. Test the evolved gas with moist red litmus paper, and note its odour. When the mass has resolidified, dissolve it in cold water and test the solution with two or three drops of sodium hydroxide and a drop of copper sulphate ; violet coloration.

(*ii*) Warm some urea with sodium hydroxide ; ammonia is evolved.

(*iii*) Prepare a solution of urea in water, acidify it with hydrochloric acid, and add sodium nitrite solution ; effervescence, due to the evolution of a mixture of nitrogen and carbon dioxide.

(*iv*) Prepare a concentrated solution of urea, divide into three parts, and test separately with (*a*) concentrated nitric acid, (*b*) saturated aqueous oxalic acid, and (*c*) 1 per cent mercuric nitrate. A white ppt. is formed in each case.

9. Estimation of Urea.—

(1) **Hufner's hypobromite method.** A simple method for the estimation of urea is by means of alkaline sodium hypobromite (*see* reaction 4, p. 412). One of the forms of the apparatus used in this method is the Doremus ureameter shown in Fig. 1.

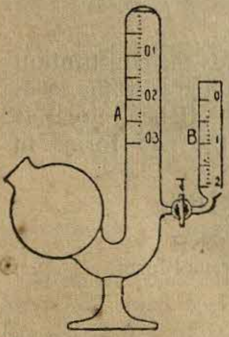


Fig. 1.
Doremus Ureameter.

The large tube, *A*, is filled with a cold, freshly prepared solution of sodium hypobromite, while the smaller tube, *B*, is charged with urine or dilute (about 2 per cent) urea solution to be examined. The tap *T* is then carefully opened and exactly 1 ml. of the urea solution is admitted. The volume of nitrogen that collects in the tube *A* is read, and gives directly the weight of urea per ml. of the liquid.

(2) **By urease.** This very convenient and accurate method is based on the hydrolytic decomposition of urea by *urease* (*see* reaction 2, above). The apparatus used in this method is shown in Fig. 2.

In the tall cylinder, *B*, are placed 1 gm. of powdered soya beans, 5 ml. of the urea solution (1 to 2 per cent), 25 ml. of water, and about 2 ml. of liquid paraffin. The contents are kept warm by placing *B* in a water-bath at 40°. The receiving bottle, *C*, contains 50 ml. of sulphuric acid coloured with a few drops of methyl orange. A current of air is drawn through the apparatus by means of a filter pump attached to *C*. The wash-bottle, *A*, contains sulphuric acid to remove ammonia from the air. The ammonia formed by the decomposition of urea is caught in the standard acid in *C*. When the air has been passing through the apparatus for about one hour, 1 gm. of anhydrous sodium carbonate is put into *B* so as to liberate ammonia retained as ammonium carbonate, and the air current is continued for another half-hour. The excess of the acid in *C* is then back-titrated with N/10 NaOH, and the amount of urea in 5 ml. of the original liquid is calculated.

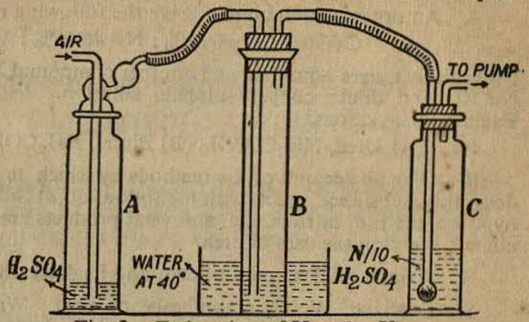


Fig. 2. Estimation of Urea by *Urease*.

10. Uses of Urea.—

(1) Synthetic urea is extensively employed as a fertilizer in agriculture.

(2) As a stabilizer of smokeless powder and other explosives.

(3) Another important application of urea is in the manufacture of urea-formaldehyde resins.

11. Urea-Formaldehyde Resins. Like phenol-formaldehyde resins (Bakelite), urea-formaldehyde resins are prepared by heating the components for a short time with a small amount of a basic catalyst (ammonia, pyridine, hexamethylenetetramine). The initial product differs from that obtained by the condensation of phenol with formaldehyde in being water soluble. It can therefore be easily applied to various materials including textiles. On heating, the resinification proceeds further with the formation of water-insoluble products. Urea-formaldehyde resins find extensive use in making unbreakable ornaments, light fittings, tableware, etc.

QUESTIONS

1. How is urea prepared ? Give its characteristic reactions, and discuss its constitution. (*Punjab, B.Sc., 1934 ; Nagpur, B.Sc., 1951*)

2. How is urea obtained on a large scale ? State its important uses. How does it react with (*a*) sodium hydroxide, (*b*) nitric acid, (*c*) nitrous acid, (*d*) alkaline hypochlorite. (*Andhra, B.Sc., 1953*)

3. 20 ml. of a liquid containing urea, on treatment with alkaline sodium hypobromite, yielded 43·05 ml. of nitrogen measured at 18° and 742 mm. pressure. Given that in this reaction only 92 per cent of the nitrogen is evolved in the gaseous state, calculate the percentage of urea in the liquid.
(*Ans.* 0·574 gm. per 100 ml.)

4. (*a*) An aqueous solution contains sodium chloride and either ammonium acetate, acetamide or urea. What tests would you use to determine which of the three latter named substances is present ?

(*b*) Write balanced equations for the reactions between urea and (*i*) sodium hypobromite, (*ii*) acetic anhydride and (*iii*) malonic ester. (*Rajasthan, B.Sc., 1954*)

5. How is urea manufactured ? How does it react with (*a*) nitrous acid, (*b*) alkaline hypobromite and (*c*) malonic ester ? (*Calcutta, First M.B.B.S., 1961*)

6. An organic compound A gave the following results on analysis :

$$C=20\% \; ; H=6{\cdot}66\% \; ; N=46{\cdot}66\% \; ; \text{Mol. wt.}=60$$

On heating it gives ammonia and another compound B that gave pink colour with NaOH and dilute copper sulphate solution. Assign structure to A and B. Explain the reactions. (*Agra, B.Sc., 1958*)

Ans. (A) Urea, NH_2CONH_2 (B) Biuret, $NH_2CONHCONH_2$.

7. Give an account of the methods by which urea may be prepared. How does this substance react with the following (*a*) Sodium hydroxide ; (*b*) Sodium hypobromite ; (*c*) nitrous acid, and what products are formed when it is heated alone ? Mention the uses of urea. (*Mysore, B.Sc., 1954*)

8. Write a brief account of urea and its derivatives. (*Ceylon, B.Sc., 1954*)

9. Describe Wohler's synthesis of urea. Write equations. Explain the changes which are induced in urea by (*a*) heat, (*b*) nitrous acid, (*c*) aqueous alkalis, (*d*) nitric acid. (*Gauhati, B.Sc., 1955*)

10. Discuss the constitution of urea. (*Lucknow, B.Sc., Prev., 1959*)

11. How is urea manufactured ? Discuss the constitution assigned to the compound. What is the action of (*i*) nitrous acid, (*ii*) alkaline hypobromite, and (*iii*) malonic ester on urea. (*Nagpur, B.Sc., 1957*)

12. How is urea prepared commercially ? How will you detect its presence ? Discuss also the constitution of urea. (*Rajasthan, B.Sc., 1959*)

13. How is urea manufactured ? Describe the action of (*a*) heat (*b*) nitrous acid, (*c*) malonic ester on urea.

0·4 gm. of a sample of impure urea on treatment with alkaline sodium hypobromite gave 112·0 c.cs. of nitrogen at N.T.P. Calculate the purity of the given sample of urea. (*Rajasthan, B.Sc., 1960 ; Delhi, B.Sc., 1960*)

Ans. 75 per cent.

14. Why urea is called carbamide ? Discribe the products obtained by the action of following reagents on urea :

(*a*) Nitrous acid ; (*b*) Caustic soda ; and (*c*) Bromine in caustic soda. (*Lucknow, B.Sc., 1951*)

CHAPTER TWENTY-SIX

ALDEHYDIC AND KETONIC ACIDS

These acids contain, in addition to the carboxyl group, the aldehyde group or the keto group. Hence they possess the dual character of carboxylic acids and aldehydes or ketones.

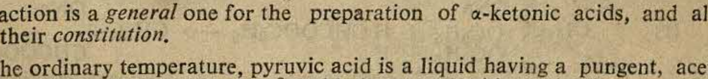
1. **Glyoxalic Acid** (or *Glyoxylic Acid*),

$$CHO.COOH.H_2O, \text{ or } \begin{matrix}HO\\HO\end{matrix}{>}CHCOOH.$$

This is the first and the best known member of the series of aldehydic acids. It is present in young plants and unripe fruits (*e.g.*, gooseberries). It may be obtained synthetically from dichloro- or dibromo-acetic acid by heating with water. It possesses the usual properties of an aldehyde, and reduces ammoniacal silver solution, forms sodium bisulphite addition compound, and an oxime. When boiled with an alkali, it yields glycollic and oxalic acids, (compare formaldehyde).

$$2CHO.COOH + H_2O \longrightarrow CH_2OH.COOH + HOOC.COOH$$

2. **Pyruvic Acid.** *α-Ketopropionic Acid*, $CH_3.CO.COOH$.—This is the first member of the series of monobasic ketonic acids. It is obtained by distilling tartaric acid or racemic acid with potassium hydrogen sulphate. The reaction is supposed to occur in two stages :



$$\begin{matrix}CH(OH)COOH\\ |\\ CH(OH)COOH\end{matrix} \xrightarrow{-CO_2} \begin{matrix}CH_2OH\\ |\\ CH(OH)COOH\end{matrix} \xrightarrow{-H_2O} \begin{matrix}CH_3\\ |\\ COCOOH\end{matrix}$$

Tartaric acid　　Glyceric acid　　Pyruvic acid

Pyruvic acid may be *synthesized* from acetyl chloride through acetyl cyanide :

$$CH_3COCl \xrightarrow{KCN} CH_3COCN \xrightarrow{HOH} CH_3COCOOH$$

This reaction is a *general* one for the preparation of α-ketonic acids, and also proves their *constitution*.

At the ordinary temperature, pyruvic acid is a liquid having a pungent, acetic acid-like odour. It solidifies at 9° and boils at 165° with partial decomposition. The acid is soluble in water in all proportions.

Owing to the immediate proximity of the carboxyl to the negative carbonyl group, pyruvic acid is much stronger (over 400 times) than acetic acid. It has the usual reactions of a ketone, and forms an oxime, a phenylhydrazone and a cyanohydrin.

3. **Acetoacetic Acid**, *β-Keto-butyric Acid*, CH_3COCH_2COOH.—This acid occurs in the urine of diabetic patients. It may be obtained as a viscous liquid by hydrolysing the ester with cold dilute alkali. It is very unstable, and readily decomposes into acetone and carbon dioxide. The acid itself is not of much importance.

4. **Ethyl Acetoacetate**, Acetoacetic Ester, $CH_3COCH_2COOC_2H_5$. The ethyl ester of acetoacetic acid, commonly called **acetoacetic ester**,

is one of the most important reagents employed in synthetic organic chemistry. It is also of considerable theoretical interest as presenting a classical example of **keto-enol tautomerism.**

Preparation. The reaction by which acetoacetic ester is prepared consists in the condensation of *two* molecules of ethyl acetate under the influence of a basic catalyst (metallic sodium or sodium ethoxide). One of the molecules acts as the **acylating agent** and the other as the **hydrogen-active methylene component** :—

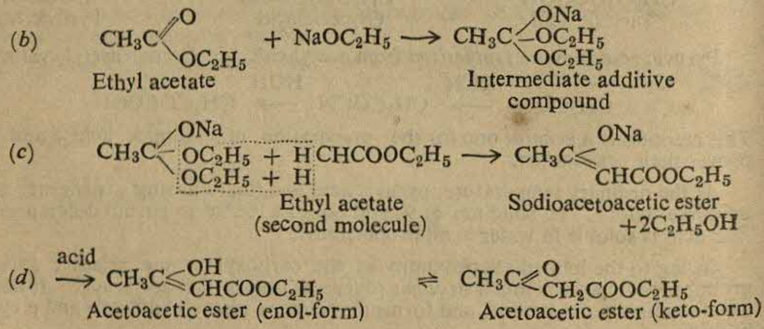
$$CH_3CO\vdots OC_2H_5 + H\vdots CH_2COOC_2H_5 \rightarrow CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

A molecule of alcohol is eliminated between the $—OC_2H_5$ group of the acylating molecule and a hydrogen atom of the other molecule in the *alpha* position, as shown in the above equation.

The reaction is usually carried out by refluxing dry ethyl acetate (10 parts) with fine sodium wire (1 part). When the reaction is over, the semi-solid product containing sodio-derivative of acetoacetic ester is acidified. The oily layer of the liberated ester is separated and purified by distillation under reduced pressure.

Claisen's Theory of the Reaction. According to the theory put forward by Claisen (1887), **sodium ethoxide**[1], formed by the action of sodium on traces of alcohol contained in the ester, **acts as an additive catalyst** in the above reaction. The different stages of the reaction are as follows :

(*a*) $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$



(*b*) $CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OC_2H_5\end{matrix} + NaOC_2H_5 \longrightarrow CH_3C\begin{matrix}\diagup ONa\\ \angle OC_2H_5\\ \diagdown OC_2H_5\end{matrix}$

Ethyl acetate — Intermediate additive compound

(*c*) $CH_3C\begin{matrix}\diagup ONa\\ \angle OC_2H_5 + H\,CHCOOC_2H_5\\ \diagdown OC_2H_5 + H\end{matrix} \longrightarrow CH_3C\begin{matrix}\diagup ONa\\ \diagdown CHCOOC_2H_5\end{matrix} + 2C_2H_5OH$

Ethyl acetate (second molecule) — Sodioacetoacetic ester

(*d*) $\xrightarrow{\text{acid}} CH_3C\begin{matrix}\diagup\!\!\diagup OH\\ \diagdown CHCOOC_2H_5\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown CH_2COOC_2H_5\end{matrix}$

Acetoacetic ester (enol-form) — Acetoacetic ester (keto-form)

Physical Properties. Acetoacetic ester is a colourless liquid having a pleasant fruity odour, and boiling at 181° with slight decomposition. It is sparingly soluble in water but readily so in alcohol and ether.

Reactions. The following three are the most important reactions of acetoacetic ester :—

(1) **Formation of Sodio-derivatives.** The hydrogen atoms of the

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[1] Claisen proved that alcohol-free ethyl acetate does *not* react with sodium in the cold.

CH_2 group in acetoacetic ester, like those in malonic ester, can be successively replaced by sodium.[1]

(2) **Ketonic Hydrolysis.** When acetoacetic ester is treated with *dilute* alkali in the cold, followed by acidification and boiling, it undergoes hydrolysis and decarboxylation, yielding acetone :—

$$\mathrm{\underset{+H}{CH_3COCH_2}\,COO\,\underset{OH}{C_2H_5}} \longrightarrow \mathrm{CH_3COCH_3 + CO_2 + C_2H_5OH}$$

Alkyl derivatives of acetoacetic ester behave in the same way, giving *ketones* ; hence the name "*ketonic hydrolysis*".

(3) **Acid Hydrolysis.** When the ester is heated with very concentrated alcoholic potash, acetic acid (two molecules) and alcohol (one molecule) are produced :—

$$\mathrm{\underset{+OH}{CH_3CO}\,\underset{H}{CH_2}.\underset{+\ H}{COO}\,\underset{OH}{C_2H_5}} \rightarrow \mathrm{CH_3COOH + CH_3COOH + C_2H_5OH}$$

Alkyl- and dialkyl-acetoacetic esters behave similarly, with the production of acetic acid (one molecule) and another fatty acid (one molecule) ; hence the name "*acid hydrolysis*".

5. **Synthetic Applications of Acetoacetic Ester.**—The above three reactions render acetoacetic ester one of the most important synthesizing agents. The following are the more important of the acetoacetic ester syntheses :

(1) **Mono- and di-alkyl acetoacetic esters.** These can be obtained as follows :—

$$\begin{aligned}
&\underset{\text{Acetoacetic ester}}{\mathrm{CH_3COCH_2COOC_2H_5}} \xrightarrow{\mathrm{C_2H_5ONa}} \underset{\text{Sodio-acetoacetic ester}}{\mathrm{CH_3COCHNaCOOC_2H_5}}\\
&\xrightarrow{\mathrm{RI}} \underset{\substack{\text{Monalkyl-}\\ \text{acetoacetic ester}}}{\mathrm{CH_3COCHRCOOC_2H_5}} \xrightarrow{\mathrm{C_2H_5ONa}} \underset{\substack{\text{Sodio-derivative of}\\ \text{monalkyl-acetoacetic ester}}}{\mathrm{CH_3COCRNaCOOC_2H_5}}\\
&\qquad\qquad\qquad\qquad\qquad \xrightarrow{\mathrm{R'I}} \underset{\text{Dialkyl-acetoacetic ester}}{\mathrm{CH_3COCRR'COOC_2H_5}}
\end{aligned}$$

The importance of these mono- and di-alkyl acetoacetic esters lies in the fact that, like acetoacetic ester itself, they yield ketones and acids on hydrolysis.

(2) **Ketones.** When an alkyl- or diakyl-acetoacetic ester, prepared as above, is submitted to **ketonic hydrolysis** (treatment with *dilute* alkali followed by acidification and boiling), we get a ketone of the form $CH_3—CO—CH_2R$ or $CH_3—CO—CHR_2$; *e.g.*,

$$\mathrm{\underset{+H}{CH_3COCH(CH_3)}\,COO\,\underset{OH}{C_2H_5}} \rightarrow \underset{\substack{\text{Methyl ethyl}\\ \text{ketone}}}{\mathrm{CH_3COCH_2CH_3}} + \mathrm{CO_2 + C_2H_5OH}$$

$$\mathrm{\underset{+H}{CH_3COC(CH_3)_2}\,COO\,\underset{OH}{C_2H_5}} \rightarrow \underset{\substack{\text{Methyl isopropyl}\\ \text{ketone}}}{\mathrm{CH_3COCH(CH_3)_2}} + \mathrm{CO_2 + C_2H_5OH}$$

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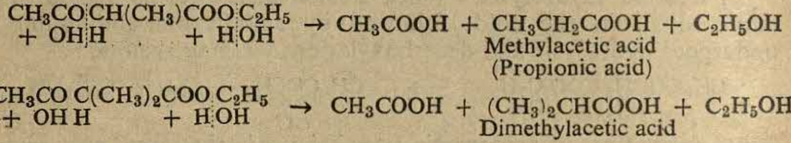
[1] It is, however, not possible to replace the second hydrogen atom by sodium, unless the first one has been replaced by an alkyl group.

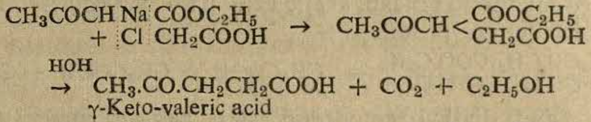
(3) **Mono- and di-alkyl acetic acids**. These are prepared by heating mono- and dialkyl-acetoacetic esters with concentrated alcoholic potash (**acid hydrolysis**) ; *e.g.*,



$$\underset{+\ OH\ H\qquad\quad +\ H\ OH}{CH_3CO\,CH(CH_3)COO\,C_2H_5} \rightarrow CH_3COOH + \underset{\substack{\text{Methylacetic acid}\\\text{(Propionic acid)}}}{CH_3CH_2COOH} + C_2H_5OH$$

$$\underset{+\ OH\,H\qquad\quad +\ H\,OH}{CH_3CO\,C(CH_3)_2COO\,C_2H_5} \rightarrow CH_3COOH + \underset{\text{Dimethylacetic acid}}{(CH_3)_2CHCOOH} + C_2H_5OH$$

(4) **γ-Ketonic acids.** These can be obtained by using *alpha*-chloro-fatty acids instead of alkyl halides in reaction (1), and submitting the product to ketonic hydrolysis ; *e.g.*,



$$\underset{+\ Cl\ CH_2COOH}{CH_3COCH\,Na\,COOC_2H_5} \rightarrow CH_3COCH{<}^{COOC_2H_5}_{CH_2COOH}$$

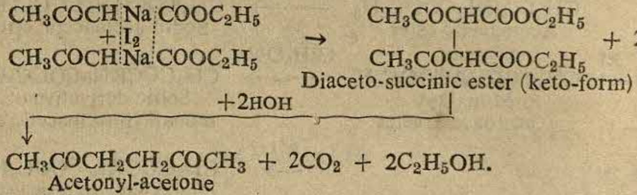
$$\xrightarrow{HOH} \underset{\gamma\text{-Keto-valeric acid}}{CH_3.CO.CH_2CH_2COOH} + CO_2 + C_2H_5OH$$

(5) **Hydrocarbons.** When acetoacetic ester and its alkyl derivatives are submitted to **electrolytic reduction**, they yield hydrocarbons, *e.g.*,

$CH_3COCH_2COOC_2H_5 \rightarrow CH_3CH_2CH_2CH_3$
Acetoacetic ester *n*-Butane

$CH_3COCH(CH_3)COOC_2H_5 \rightarrow CH_3CH_2CH(CH_3)CH_3$
Methyl-acetoacetic ester 2-Methyl-butane

(6) **Diaceto-succinic ester and acetonyl-acetone.** When sodio-acetoacetic ester is treated with iodine, two molecules of the ester condense together with production of diaceto-succinic ester, which, on ketonic hydrolysis, yields acetonylocetone (hexane-2,5-dione) :

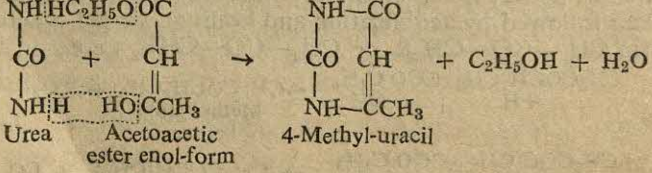


$$\begin{matrix} CH_3COCH\,Na\,COOC_2H_5 \\ +\ I_2 \\ CH_3COCH\,Na\,COOC_2H_5 \end{matrix} \rightarrow \begin{matrix} CH_3COCHCOOC_2H_5 \\ | \\ CH_3COCHCOOC_2H_5 \end{matrix} + 2NaI$$

Diaceto-succinic ester (keto-form)

$$\xrightarrow{+2HOH} \underset{\text{Acetonyl-acetone}}{CH_3COCH_2CH_2COCH_3} + 2CO_2 + 2C_2H_5OH.$$

(7) **Heterocyclic compounds.** Acetoacetic ester undergoes condensation with certain nitrogen compounds, such as ammonia, amines, amides, hydrazines and hydroxylamine. These reactions have proved very valuable for synthesizing a variety of heterocyclic compounds. Thus, with urea the following reaction occurs :



Urea Acetoacetic ester enol-form 4-Methyl-uracil

6. Constitution of Acetoacetic Ester (**Keto-enol Tautomerism**).— Acetoacetic ester shows the dual character of a keto-compound and an unsaturated hydroxy-compound. Its decomposition by dilute acids (*ketonic hydrolysis*), whereby acetone, carbon dioxide and ethyl alcohol are formed (sec. 4), is best explained by assuming the ketonic formula, $CH_3COCH_2COOC_2H_5$. This view, first put forward by Frankland, is supported by the reactions of the ester with *sodium bisulphite*, *hydrogen cyanide*, *hydroxyamine* and *phenylhydrazine*, in all of which it behaves in the same manner as a ketone. On the other hand, the formation of the *sodio-derivative* points to the presence of a hydroxyl group in the molecule, *i.e.*, the ester may have the structure $CH_3C(OH){=}CHCOOC_2H_5$. This view is supported by the fact that the ester, like phenols, gives a reddish violet coloration with *ferric chloride*. Further, it combines with *bromine*, after the manner of an unsaturated compound, yielding a dibromide.

From the above, it might be concluded that acetoacetic ester is a *tautomeric substance*, and consists of an equilibrium mixture of the ketonic and enolic forms :

$$\underset{\text{Keto-form}}{CH_3COCH_2COOC_2H_5} \rightleftharpoons \underset{\text{Enol-form}}{CH_3C(OH){=}CHCOOC_2H_5}$$

A reagent reacting exclusively with one of the forms would cause the continuous shifting of the equilibrium with production of more and more of that form, until finally the whole of the substance has reacted.

The *molecular refraction* and other physical constants of the ester show that it consists of a mixture of the two forms.

A ready method of establishing the percentage of the enol-form, under given conditions, is by direct titration with bromine. Under ordinary conditions, the liquid ester contains only about 7 per cent of the enolic form. The relative proportions of the two forms change considerably with a change of solvent. The following table shows the percentage of the enolic form in various solvents at 18° as determined by titration with bromine.

Solvent	*Percentage of enolic form*
Water	4.4
Ethyl alcohol	15.3
Ether	27.1
Carbon disulphide	32.4
Hexane	46.4

From his researches on the desmotropy of diacetosuccinic ester, Knorr came to the conclusion that the rate of isomerization of the two forms of acetoacetic ester should be slow, and that consequently a **separation** should be possible at low temperatures. Guided by this idea, he succeeded, in 1911, in actually isolating each of the two forms in a state of freedom from the other. The work was conducted at −78°[1], and extraordinary precautions were taken to avoid the introduction of foreign substances (such as cigarette smoke, HCl, and even impure laboratory air) which act catalytically and bring about immediate isomerization.

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[1] Obtained by using a freezing mixture of ether and solid carbon dioxide.

The **keto-form** was obtained by freezing it out at −78°, and crystallizing it at that temperature from alcohol. It forms long, colourless needles, melting at −39°. At low temperatures, it gives no coloration with ferric chloride, although at ordinary temperatures the test is positive, owing to rapid isomerization caused by the reagent.

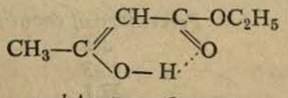
The pure **enol-form** was obtained by the action of an equivalent quantity of anhydrous hydrogen chloride on a suspension of the sodio-derivative in light petroleum at −78°, followed by filtration of the sodium chloride and evaporation of the solvent at a low temperature. It is a colourless, oily liquid at −78° and, even at that temperature, immediately reacts with ferric chloride.

A more recent method of effecting the separation of the two tautomerides is by **fractional distillation of the ester in vacuo,** a quartz flask being used to avoid enolization by the alkali present in glass.

At ordinary temperatures, and more rapidly in the presence of catalysts, either of the forms changes into the equilibrium mixture, the change being far more rapid in the case of the enol, than in that of the keto form.

Hydrogen Bonding in enol-Acetoacetic Ester.—

The greater volatility of the enol-form of acetoacetic ester, as compared with the keto-form, is noteworthy from the theoretical point of view. This is just the opposite of what one may ordinarily expect, as the alcohols are highly associated in the liquid state and boil about 30° higher than ketones of comparable molecular weight. The greater volatility of the hydroxy-form of acetoacetic ester indicates that this form differs from alcohols in being **incapable of association.** The phenomenon finds ready explanation by assuming the formation of a **'hydrogen bond'** between the hydroxyl-group and the keto-group of the ester component of the molecule, as formulated below:



enol-Acetoacetic ester

QUESTIONS

1. What is pyruvic acid ? How may it be synthesized ? Why is it a stronger acid than propionic acid ?

2. Give the preparation, synthetic uses and properties of acetoacetic ester. Discuss its constitution. (*Punjab, B.Sc., 1954*)

3. How is ethyl acetoacetate prepared ? What is the mechanism of its formation ? Starting with this ester, indicate the steps involved in the preparation of :

(*a*) methyl *n*-butyl ketone, $CH_3CO(CH_2)_3CH_3$,
(*b*) *n*-propylethylacetic acid, $CH_3CH_2CH_2(CH_3CH_2)CHCOOH$,
(*c*) *n*-butyric acid, $CH_3CH_2CH_2COOH$ (*Banaras, B.Sc., 1954*)

4. "Acetoacetic ester is an equilibrium mixture of the keto and enol modifications." On what evidence is the above statement based ? Starting from the ester, indicate how the following may be synthesised :

(*a*) *n*-Butyric acid, (*b*) Succinic acid, and (*c*) Methyl ethyl ketone. (*Delhi, B.Sc., 1951*)

5. Acetoacetic ester behaves sometimes as a keto compound and sometimes as an unsaturated hydroxy compound. What explanation can you offer for this apparent contradiction ? (*Delhi, B.Sc., 1954*)

6. How is ethyl aceteacetate used in organic synthesis ? Discuss the chemical constitution of ethyl acetoacetate. (*Nagpur, B.Sc., 1954*)

7. Give the synthetic uses of Acetoacetic ester. (*Lucknow, B.Sc., 1961*)

8. Discuss the structure of acetoacetic ester. Show how the tautomeric forms of it are separated and estimated from their equilibrium mixture. (*Bombay, B.Sc., 1955*)

9. (*a*) How can Ethyl acetoacetate be prepared ?

(*b*) Give the procedure by which the following compounds may be obtained from Ethyl acetoacetate :

(*i*) Methyl ethyl ketone. (*ii*) Acetonyl acetone.
(*iii*) 2,3-Dimethylbutyric acid. (*Punjab, B.Sc., 1963*)

10. Describe the preparation of ethyl acetoacetate. Show how you would obtain (*a*) isobutyric acid, (*b*) methyl propyl ketone, starting from ethyl acetoacetate. (*Agra, B.Sc., 1960*)

11. How is ethyl acetoacetate prepared ? Discuss its tautomerism. Explain how it is used for the synthesis of methyl ethyl ketone and isobutyric acid. (*Andhra, B.Sc., 1958*)

12. Give the preparation and synthetic uses of ethyl acetoacetate. (*Bombay, B.Sc., Chemistry* (*Principal*), *1957, 1963*)

13. Describe, giving equations, the preparation of ethyl acetoacetate. State its characteristic properties and illustrate with typical examples its various uses in synthesis. (*Calcutta, B.Sc., 1961*)

14. Describe the preparation and synthetical uses of ethyl- acetoacetate. (*Punjab, B.Sc., 1962*)

15. Explain the principles underlying the synthetic applications of ethyl acetoacetate. Starting with this how will you prepare (*a*) succinic acid, (*b*) 2-methylbutane and (*c*) acetonylacetone. (*Punjab, B.Sc., Chem. Engg., 1963*)

16. How is acetoacetic ester prepared ? Using this ester, show how the following compounds may be synthesised :—

(*a*) Isobutyric acid, (*b*) Active valeric acid, (*c*) Methyl isopropyl ketone and (*d*) Acetonylacetone. (*Punjab, B.Sc., 1957*)

17. How is ethyl acetoacetate prepared ? Write an account of its uses in synthetic organic chemistry. (*Jammu & Kashmir, B.Sc., 1960*)

18. How is ethyl acetoacetate obtained ? Give an account of the various syntheses in which it has been used. (*Jammu & Kashmir, B.Sc., 1957*)

19. Discuss the importance of ethyl acetoacetate in synthetic organic chemistry. (*Karachi, B Sc., 1957*)

20. Bring out clearly how acetoacetic ester is of great value in synthetic organic chemistry. (*Karnatak, B.Sc., 1961*)

21. Describe the preparation of acetoacetic ester and outline its uses in synthetic organic chemistry. (*Saugar, B.Sc., 1961*)

22. How is ethyl acetoacetate prepared ? Give an account of its synthetic applications. (*Osmania, B.Sc., 1959*)

23. What structural property of acetoacetic ester makes it a valuable reagent? Give the synthetic uses of the ester. (*Osmania, B.Sc., 1956*)

24. Give an account of the phenomenon of tautomerism, taking the help of the chemistry of acetoacetic ester. Starting from the ester, indicate, by equations, how succinic acid and *n*-butyric acid may be synthesised. (*Rajasthan, B.Sc., 1957*)

25. Describe the preparation of acetoacetic ester. Discuss its constitution. How will you obtain any four of the following compounds by the use of acetoacetic ester :

(*i*) ethylpropylacetic acid,
(*ii*) methyl amyl ketone,
(*iii*) crotonic acid,
(*iv*) methyl uracil,
(*v*) antipyrine,
(*vi*) 1 : 4 diketone ?

(*Poona, B.Sc., 1958*)

26. How is ethyl acetoacetate prepared in the laboratory ? Discuss its constitution. Using ethyl acetoacetate, how would you synthesise the following :—

(*a*) *n*-butyric acid, (*b*) *iso*-butyric acid and (*c*) levulinic acid ?

(*Travancore, B.Sc., 1956*)

27. Saturated alcohols of the aliphatic series boil about 30° higher than ketones of comparable molecular weight, while *enol*-acetoacetic ester is more volatile than its *keto*-form. How do you explain this anomaly ?

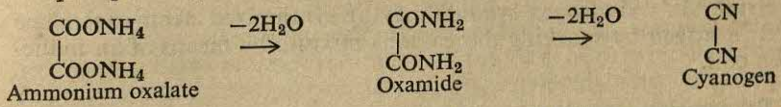
CHAPTER TWENTY-SEVEN

CYANOGEN COMPOUNDS

General. The compounds derived from cyanogen, $(CN)_2$, are termed **cyanogen compounds** in the same way as the compounds containing chlorine are called "chlorine compounds". Many of the cyanogen compounds are of importance in synthetic organic chemistry.

1. Cyanogen, *Oxalonitrile*, $N{\equiv}C{-}C{\equiv}N$.

Preparation. (1) Being the nitrile of oxalic acid, cyanogen may be obtained from ammonium oxalate or oxamide by heating them with phosphorus pentoxide:



$$\underset{\text{Ammonium oxalate}}{\begin{array}{c}COONH_4\\|\\COONH_4\end{array}} \xrightarrow{-2H_2O} \underset{\text{Oxamide}}{\begin{array}{c}CONH_2\\|\\CONH_2\end{array}} \xrightarrow{-2H_2O} \underset{\text{Cyanogen}}{\begin{array}{c}CN\\|\\CN\end{array}}$$

In this reaction, a brown, amorphous polymeride, known as **paracyanogen**, $(CN)_x$, is left behind, which on further heating yields cyanogen.

(2) The gas is readily prepared by heating mercuric cyanide, the reaction by which it was discovered by Gay-Lussac:—

$$Hg(CN)_2 \longrightarrow Hg + (CN)_2$$

Expt. 1. Heat some mercuric cyanide in a test-tube, and ignite the evolved gas at the mouth of the tube. It will be found to burn with a purple flame. A brown, amorphous residue of paracyanogen will remain in the tube.

(3) Perhaps the most convenient method of preparing cyanogen in the laboratory consists in heating a solution of cupric sulphate with potassium cyanide, cuprous cyanide being precipitated at the same time. The reaction is due to reduction of the cupric ion to the cuprous ion by the cyanide ion :—

$$2Cu^{++} + 4CN^- \longrightarrow 2CuCN + (CN)_2$$

Expt. 2. Heat a solution of cupric sulphate with potassium cyanide, and ignite the evolved gas at the mouth of the tube

Properties. (1) Cyanogen is a colourless gas with a characteristic pungent odour and is extremely poisonous. Under a pressure of four atmospheres, it can be condensed to a liquid, which boils at −20° and solidifies at −34°. Cyanogen is readily soluble in water, but the solution is unstable (*see* below).

(2) Cyanogen is combustible, and burns in air with a violet flame, producing carbon dioxide and nitrogen:

$$(CN)_2 + 2O_2 \longrightarrow 2CO_2 + N_2$$

(3) When cyanogen is dissolved in hydrochloric acid, it takes up four molecules of water, yielding oxalic acid and ammonia (ammonium oxalate) :

$$(CN)_2 + 4H_2O \longrightarrow (COOH)_2 + 2NH_3 \longrightarrow (COONH_4)_2$$

(4) When reduced with tin and hydrochloric acid, cyanogen yields ethylene diamine:

$$N{\equiv}C{-}C{\equiv}N + 8H \longrightarrow H_2N{-}CH_2{-}CH_2{-}NH_2$$

2. **Hydrogen Cyanide,** Hydrocyanic Acid, *Prussic Acid*, HCN.—This compound occurs in the free state in certain plants, and as the glucoside *amygdalin* in bitter almonds. Amygdalin is decomposed as follows by the hydrolytic action of the enzyme *emulsin*, also present in bitter almonds:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCN + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Synthesis. Hydrogen cyanide may be synthesized from acetylene and nitrogen by sparking the gaseous mixture by means of an induction coil.

Preparation :—

(1) **From Sodium Cyanide.** Hydrogen cyanide is most conveniently prepared by adding concentrated sulphuric acid, diluted with its own volume of water, to a warm, concentrated aqueous solution of sodium cyanide,

$$2NaCN + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCN$$

The hydrocyanic acid comes off as a gas, and is liquefied by means of freezing mixture.

(2) **From Formamide.** A large proportion of commercial HCN is obtained by the catalytic dehydration of formamide:—

$$HCONH_2 \longrightarrow HCN + H_2O$$

(3) **From Methane and Ammonia.** Much hydrogen cyanide is also obtained by catalytic pyrolysis of a mixture of methane and ammonia.

$$CH_4 + NH_3 \xrightarrow{1000°,\ Pt} HCN + 3H_2.$$

(4) **From Beet-sugar Molasses.** Hydrogen cyanide is also obtained as a by-product of beet-sugar industry. Sugar-beet contains some betain (trimethylglycine), which collects in the molasses. The destructive distillation of the molasses gives trimethylamine. The latter when passed through fireclay tubes heated at 800°—1000° undergoes pyrolysis into methane and hydrogen cyanide:—

$$\underset{\text{Betain}}{(CH_3)_3\overset{+}{N}CH_2COO^-} \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} \longrightarrow 2CH_4 + HCN$$

Properties. (1) Anhydrous hydrogen cyanide is a colourless liquid with an odour of bitter almonds. It boils at 26°, and solidifies at −14°.

(2) Hydrogen cyanide is *excessively poisonous*, and greatest care must be taken in handling it.

(3) Hydrogen cyanide is one of the weakest acids. It gives rise to metallic salts, called cyanides, and two kinds of alkyl derivatives, *viz.*, cyanides and isocyanides.

(4) When treated with concentrated hydrochloric acid, it is rapidly decomposed, with rise of temperature, first into formamide, and then into formic acid and ammonia:

$$HCN \xrightarrow{+H_2O} HCONH_2 \xrightarrow{HOH} HCOOH + NH_3$$

The ammonia, of course, would combine with the excess of hydrochloric acid to form ammonium chloride.

(5) When reduced with alcohol and metallic sodium, it yields methylamine:

$$HCN + 4H \longrightarrow CH_3NH_2$$

(6) Hydrogen cyanide directly combines with all compounds containing a carbonyl group, yielding **cyanohydrins.** This reaction makes hydrogen cyanide an important reagent in synthetic organic chemistry. Thus, it is used in the preparation of hydroxy-acids and of amino-acids, and forms the basis of Kiliani's synthesis of a higher from a lower aldose.

Uses. (1) Hydrocyanic acid is used as a reagent in synthetic organic chemistry [see reaction (6) above].

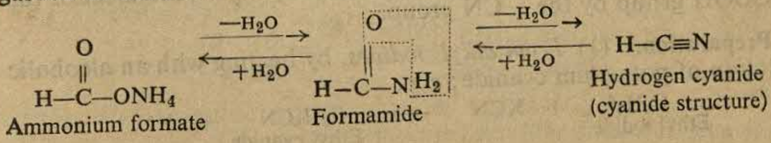
(2) The most important commercial use of hydrogen cyanide is in the preparation of acrylic and methacrylic esters (used in the manufacture of colourless, transparent plastics and as additives for lubricants) and acrylonitrile (used in the manufacture of the synthetic rubber Buna-N).

(3) Hydrocyanic acid, being one of the most deadly poisons, is used as a fumigant to exterminate rats and insects. As such, it has proved especially useful for orange orchards, holds of ship and for flour mills.

(4) Sodium cyanide finds extensive use in the metallurgy of gold and silver, and in electroplating.

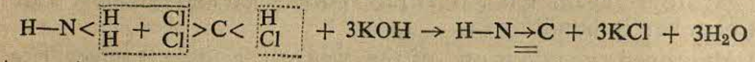
Constitution of Hydrogen Cyanide :—

(1) The formation of hydrogen cyanide by the dehydration of ammonium formate, or of formamide, and its reconversion into these substances by hydrolysis indicate that the compound must be regarded as the nitrile of formic acid having the **cyanide structure.**



$$\underset{\text{Ammonium formate}}{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONH_4} \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} \underset{\text{Formamide}}{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} \underset{\substack{\text{Hydrogen cyanide}\\ \text{(cyanide structure)}}}{H{-}C{\equiv}N}$$

(2) On the other hand, its formation by the well-known *carbylamine reaction* (*i.e.*, by heating a mixture of ammonia, chloroform and alcoholic potash) indicates the **isocyanide structure,**



$$H{-}N{<}\begin{smallmatrix}H\\H\end{smallmatrix} + \begin{smallmatrix}Cl\\Cl\end{smallmatrix}{>}C{<}\begin{smallmatrix}H\\Cl\end{smallmatrix} + 3KOH \rightarrow H{-}N\underset{=}{\rightarrow}C + 3KCl + 3H_2O$$

Ammonia chloroform

(3) Hydrogen cyanide gives two distinct series of alkyl derivatives:

$R{-}C{\equiv}N$ and $R{-}N\underset{=}{\rightarrow}C$

cyanides isocyanide

(4) The Raman spectra of hydrogen cyanide show two distinct bands, one corresponding to that exhibited by alkyl cyanides and the other to the one that characterizes alkyl isocyanides. The former is very much stronger than the latter, and from their relative intensities it has been estimated that the HCN form constitutes 99.5 per cent and the HNC form 0.5 per cent.

Hence, we see that hydrogen cyanide is a **tautomeric substance** consisting of the interconvertible cyanide and isocyanide forms:

$$\underset{\text{(99.5 per cent)}}{H{-}C{\equiv}N} \rightleftharpoons \underset{\text{(0.5 per cent)}}{H{-}N\underset{=}{\rightarrow}C}$$

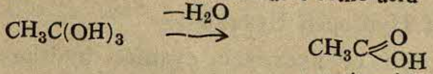
The conversion of one form into the other occurs through, what is termed, **prototropy**, *i.e.*, by the shift of a proton, or hydrogen ion, from one atom to the next:—

$$H{-}C{\equiv}N + H^+ \rightleftharpoons [H{-}\overset{+}{C}{=}N{-}H]^+ \rightleftharpoons H^+ + C\underset{=}{\leftarrow}N{-}H$$

In the conversion of the cyanide into the isocyanide form, a proton attacks one of the lone pairs of electrons on the nitrogen atom and immediately another proton is expelled from the carbon. The isocyanide-to-cyanide conversion occurs through the reversal of this process.

3. Alkyl Cyanides or Acid Nitriles, $R{-}C{\equiv}N$.—These compounds differ from esters of other acids in the fact that the alkyl group is linked to *carbon*. Hence, on hydrolysis, they do not yield the corresponding alcohols and hydrogen cyanide but carboxylic acids containing the same number of carbon atoms as the ester itself; *e.g.*,

$$\underset{\text{Methyl cyanide}}{CH_3C{\equiv}N} + 3HOH \longrightarrow \underset{\text{unstable ortho-acid}}{CH_3C(OH)_3} + NH_3$$



$$CH_3C(OH)_3 \xrightarrow{-H_2O} CH_3C{\lessgtr}\begin{smallmatrix}O\\OH\end{smallmatrix}$$

acetic acid

For this reason, they are termed the *nitriles* of carboxylic acids, and are regarded as derived from the latter by the replacement of the $-COOH$ group by the $-CN$ group.

Preparation. (1) *From alkyl iodides*, by heating with an alcoholic solution of potassium cyanide; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KCN \longrightarrow \underset{\text{Ethyl cyanide}}{C_2H_5CN} + KI$$

(2) *From alkyl potassium sulphate*, by distilling with dry potassium cyanide:

$$C_2H_5KSO_4 + KCN \longrightarrow C_2H_5CN + K_2SO_4$$

(3) *From amides*, by distilling with a dehydrating agent (thionyl chloride or phosphorus pentoxide):—

$$\underset{\text{Acetamide}}{CH_3CONH_2} + SOCl \longrightarrow \underset{\text{acetonitrile}}{CH_3CN} + SO_2 + 2HCl$$

$$CH_3CONH_2 + P_2O_5 \longrightarrow CH_3CN + 2HPO_3$$

(4) *From Ammonium Salts of Carboxylic Acids.* The industrial method for preparing nitriles consists in a single-stage dehydration of ammonium salts. The vapour of the carboxylic acid and ammonia is passed over heated alumina at about 500°,

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{-H_2O} CH_3CONH_2 \xrightarrow{-H_2O} CH_3CN$$

Methods 3 and 4 for the preparation of alkyl cyanides show that they are to be regarded as derivatives of carboxylic acids; hence, the name **acid nitriles** or simply **nitriles.**

Properties. The lower members are colourless liquids, with a strong sweetish smell and a poisonous action. They are moderately soluble in water.

The important **reactions of alkyl cyanides** are :

(1) *Addition of Water.* When treated with moderately concentrated sulphuric acid, a molecule of water is added and an amide is formed :

$$\underset{\text{Acetonitrile}}{CH_3C{\equiv}N} + H_2O \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

(2) *Hydrolysis.* When boiled with an alkali or dilute mineral acid, an alkyl cyanide is hydrolysed to give a fatty acid and ammonia :

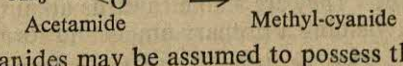
$$CH_3CN + 2H_2O \longrightarrow CH_3COOH + NH_3$$

(3) *Reduction.* When reduced with lithium aluminium hydride, or sodium amalgam and alcohol, alkyl cyanides are converted into primary amines ; *e.g.*,

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 4H \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

(4) *Addition with Grignard reagents*, followed by hydrolysis, results in the production of ketones. (See chap. 13, sec. 4, reaction 2, vii, p. 218).

Constitution. The constitution of alkyl cyanides follows from their formation from acid amides. Thus, in acetamide the two carbon atoms are known to be *directly* linked together, and we may reasonably infer that on converting the acetamide into methyl cyanide, the two carbon atoms *remain* united :



$$CH_3{-}C{\lessgtr}^{NH_2}_{O} \xrightarrow{-H_2O} CH_3{-}C{\equiv}N$$

Acetamide Methyl-cyanide

Hence, alkyl cyanides may be assumed to possess the structural formula, $R{-}C{\equiv}N$. This view is supported by their chemical behaviour (see Reactions 1, 2 and 3 given above). All the products obtained, *viz.*, the carboxylic acids, amides, and amines have the alkyl group, originally present in the cyanide, directly linked to a carbon atom.

4. Use of Alkyl Cyanides in Organic Synthesis.—Alkyl cyanides are important synthesizing agents, and are employed—

(*i*) *For the preparation of amides, carboxylic acids and primary amines.* [See Reactions 1, 2 and 3 given above].

(*ii*) *For Ascending the Series.* The formation of alkyl cyanides from alkyl halides and their reactions are utilized for ascending the series, *i.e.*, for preparing a higher member from a lower one. Thus, acetic acid may be converted into propionic acid:

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{\text{Reduction}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow{\text{Reduction}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{H+I} \underset{\text{Ethyl iodide}}{C_2H_5I}$$

$$\xrightarrow{\substack{\text{Alcoholic}\\ KCN}} \underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow{HOH} \underset{\text{Propionic acid}}{C_2H_5COOH}$$

Similarly, methyl alcohol may be converted into ethyl alcohol by the following series of reactions:—

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{\substack{\text{Iodine and}\\ \text{red phosphorus}}} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{\substack{\text{Alcoholic}\\ KCN}} \underset{\text{Methyl cyanide}}{CH_3CN}$$

$$\xrightarrow{\text{Reduction}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

5. Isocyanides, Isonitriles *or* **Carbylamines.**—These compounds are isomeric with alkyl cyanides, from which they differ in having the alkyl group attached to *nitrogen.*

Preparation. (1) By distilling an alkyl iodide with *silver* cyanide:

$$RI + AgCN \longrightarrow RNC + AgI$$

(2) By distilling a primary amine with chloroform and alcoholic potash.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

Properties. Isonitriles differ entirely from nitriles in their properties, as described below:

(1) *Physical.* They are volatile liquids, possessing extremely **disgusting odour.**

(2) *Hydrolysis.* They are stable towards alkalis, but are decomposed by acids, yielding a primary amine and formic acid:

$$RNC + 2H_2O \longrightarrow RNH_2 + HCOOH$$

(3) *Hydrogenation.* By catalytic hydrogenation, four atoms of

hydrogen are added, one to nitrogen and three to carbon, a secondary amine being formed :

$$RN\underset{=}{\rightarrow}C + 4H \longrightarrow R-NH-CH_3$$

(4) *Isomerization.* At high temperatures, alkyl isocyanides have a strong tendency to pass into the isomeric cyanides:

$$R-N\underset{=}{\rightarrow}C \longrightarrow R-C\equiv N$$

This shows that the cyanides are more stable than the isocyanides.

Constitution. The reactions 1 to 3 of isonitriles and their formation from primary amines and chloroform show that the *alkyl group is in direct union with nitrogen*, and not with carbon. Nef in 1892 postulated that the carbon of the isocyanide group is divalent, and wrote the formula of an isocyanide as $R-N=C$. A quadruple bond between nitrogen and carbon is inadmissible on stereochemical grounds, and, moreover, is inconsistent with the covalency rule of Sidgwick, which limits the covalency of nitrogen and of carbon to four.

Langmuir in 1923 suggested an alternative formula in which, in addition to' the four-electron bond postulated in the Nef formula, a co-ordinate link is assumed to exist between nitrogen and carbon, the former donating its lone pair of electrons to the latter. The octet of carbon is thus completed. The Langmuir formula, therefore, is $R-N\underset{=}{\rightarrow}C$.

Its correctness was established by Sidgwick and others in 1930 by a study of the parachors and dipole moments. The carbon in the formula has one lone pair of electrons by means of which it can coordinate as a donor, while, if the co-ordinate bond is ruptured, it can also act as an acceptor. The formula is thus in complete harmony with the chemical behaviour of isocyanides, the **carbon being the reactive centre.**

6. Cyanic Acid.—Like hydrocyanic acid, this compound yields two series of alkyl derivatives, the *cyanates* and the *isocyanates*, and is, therefore, regarded as an equilibrium mixture of the two tautomeric forms:

$$\underset{\text{Cyanic acid}}{H-O-C\equiv N} \rightleftharpoons \underset{\text{Isocyanic acid}}{H-N=C=O}$$

That the acid **consists almost entirely of the iso-form** is supported by the following facts:—

(*i*) The Raman spectrum.

(*ii*) Addition of HF and HBr gives carbamic acid halides; *e.g.*

$$H-N=C=O + HF \longrightarrow \underset{\text{Carbamyl floride}}{H_2NC{<}^{O}_{F}}$$

(*iii*) The alkyl derivatives of only the iso-form are known.

Formation. When urea is heated, a trimeric derivative of cyanic acid, called **cyanuric acid,** is formed. On distilling cyanuric acid, and cooling the vapour with freezing mixture, we get cyanic acid as a colourless liquid,

$$\underset{\text{Urea}}{3CO(NH_2)_2} \xrightarrow{-2NH_3} \underset{\text{Cyanuric acid}}{(HNCO)_3} \rightleftharpoons \underset{\text{Cyanic acid}}{3HNCO}$$

The liquid cyanic acid is stable below 0°.

Reactions:—

(1) When the flask containing the liquid is removed from the freezing mixture, it begins to boil vigorously sometimes giving out loud reports, and is soon converted into a white, amorphous solid. This consists of a mixture of **cyanuric acid** (70 per cent) and **cyamelide** (30 per cent)[1]. Both of these compounds are trimerides of cyanic acid.

(2) Above 0°C a solution of cyanic acid in water changes readily into ammonia and carbon dioxide :—

$$\begin{array}{l} H-N=C=O \\ \quad\;\; + \\ \quad\; H_2O \end{array} \longrightarrow NH_3 + CO_2$$

(3) With alcohols, the acid forms esters of carbamic acid,

$$HNCO + C_2H_5OH \longrightarrow \underset{\text{Ethyl carbamate}}{NH_2COOC_2H_5}$$

(4) With hydrazine, it gives semicarbazide,

$$H-N=C=O + \underset{\text{Hydrazine}}{NH_2NH_2} \longrightarrow \underset{\text{Semicarbazide}}{NH_2NHCONH_2}$$

7. Alkyl Isocyanates, $R—N=C=O$.—These compounds are derived from the iso-form of cyanic acid.

Preparation. Alkyl isocyanates may be prepared—

(1) By distilling alkyl iodides with silver cyanate,

$$C_2H_5I + AgNCO \longrightarrow C_2H_5NCO + AgI$$

(2) By distilling alkyl sulphate with potassium cyanate,

$$(C_2H_5)_2SO_4 + 2KNCO \longrightarrow 2C_2H_5NCO + K_2SO_4$$

(3) By the action of phosgene (carbonyl chloride) on primary amine hydrochlorides :—

$$RNH_2HCl + COCl_2 \longrightarrow RNCO + 2HCl$$

Properties. Alkyl isocyanates are volatile liquids, with a powerful stifling odour.

When treated with a dilute solution of an alkali, they decompose into carbon dioxide and a primary amine :

$$C_2H_5N=C=O + H_2O \longrightarrow C_2H_5NH_2 + CO_2$$

This reaction proves the constitution of alkyl isocyanates. It was first employed by Wurtz for the preparation of pure primary amines, absolutely free from secondary and tertiary amines.

Alkyl isocyanates gradually polymerize to form **cyanuric esters.**

---

[1] The mixture may be separated by treatment with water in which cyanuric acid is readily soluble; cyamelide is only sparingly soluble.

QUESTIONS

1. Give the preparation and properties of cyanogen. What evidence is there that this substance possesses the constitution $N\equiv C-C\equiv N$?

2. How is hydrocyanic acid prepared ? What are its important properties ? Describe the action of hydrolysing and reducing agents on this compound. (*Patna, B.Sc., 1953*)

3. Give examples of the use of hydrocyanic acid as a reagent in organic chemistry, with special reference to its action on sugars. How may this compound be used to distinguish between an aldose and a ketose ? (*Punjab, B.Sc., Hons.*)

4. Discuss the isomerism of nitriles and isonitriles. (*Agra, B.Sc., 1959*)

5. By what qualitative reactions could you distinguish between ethyl cyanide and ethyl isocyanide ? (*Punjab, B.Sc., 1943*)

6. Explain the isomerism of carbylamines and nitriles. How is each class of bodies prepared ? How can the formulae assigned to each be proved to be correct ? Write equations. (*Nagpur, B.Sc., 1953*)

7. An organic substance analysing carbon=58.5, hydrogen=7.3, nitrogen =34.1 per cent., with vapour density=20, yields on reduction a substance containing carbon=53.3 per cent. The reduced product reacts with nitrous acid to give nitrogen. Explain these reactions fully. How would any isomer of the substance behave ? How do these substances behave on hydrolysis and how would you distinguish one from the other ? (*Punjab, B.Sc., 1938*)

8. An organic compound, *A*, gave on analysis C, 65.45%, H, 9.1% and N, 25.45%. On hydrolysis, ammonia was liberated and the second substance, B, contained C, 48.4% and H, 8.1%. Calculate the formulae of A and B. Write the equation representing the hydrolysis and also discuss the structural formulae that you assign to *A*. (*Delhi, B.Sc., 1954*)

Ans. (A) C_2H_5CN ; (B) C_2H_5COOH.

9. A neutral compound containing 25.5% nitrogen after being heated with hydrochloric acid gave an acid containing 48.7% C and 8·1% H but no nitrogen.

0.2 gm. of this acid required for neutralisation 27.0 c.cs. of N/10 NaOH solution ; the vapour density of the ethyl ester=51. What is the neutral compound ? (*Rajputana, B. Sc., 1953 ; Agra, B.Sc., 1954*)

10. Give a brief survey of the evidence upon which the alkyl cyanides and isocyanides have been given different structural formulae. (*Patna, B. Sc., 1959*)

11. What are cyanides and isocyanides ? How are they obtained ? What are the products formed when

(*a*) boiling alkaline solution ;
(*b*) hot dil. mineral acid ;
(*c*) hydrogen in presence of nickel, react with them ? (*Lahore, B.Sc., 1954*)

12. How is acetonitrile prepared ? What are its important properties ? (*Madras, B.Sc., 1955*)

13. Describe the methods for the preparation of alkyl cyanides and isocyanides. Describe their properties and discuss their structure. (*Punjab, B.Sc, 1960*)

14. Discuss critically the structural formulae of alkyl cyanides and alkyl isocyanides. How can these classes of compounds be prepared and distinguished ? (*Patna, B.Sc., 1962*)

15. Two isomeric compounds, *A* and *B*, having the molecular formula C_5H_9N behaved as follows :—

(*i*) The compound *A*, on hydrolysis with boiling hydrochloric acid, gave *C* and *D*, the former having the molecular formula $C_4H_{11}N$ and the latter CH_2O_2, The compound *C* reacts with nitrous acid, acetyl chloride and benzenesulphonic chloride. The product with the last reagent was found to be soluble in KOH solution. The compound *D* reacts with $NaHCO_3$ and, when heated with concentrated sulphuric acid, evolves carbon monoxide.

(*ii*) The compound *B*, on hydrolysis with boiling HCl, gave *E*, having the molecular formula $C_5H_{10}O_2$, which evolves carbon dioxide with $NaHCO_3$ and has a neutralization equivalent 102.

What are *A*, *B*, *C*, *D* and *E* ? Explain the above reactions. (*Rajasthan, B.Sc., 1957*)

Ans.—
(*A*) C_4H_9NC (*B*) C_4H_9CN (*C*) $C_4H_9NH_2$ (*D*) HCOOH (*E*) C_4H_9COOH.

16. A substance *X* gave on analysis C, 65.45, H, 9.10 ; N, 25.45%. When it was hydrolysed, NH_3 was evolved and a second substance *Y* which on analysis gave C, 48.6 ; H, 8.1% was obtained. When *Y* was heated with sodalime, ethane was obtained. Calculate the formulæ of two substances and write the necessary equations. State the action of Na and alcohol on *X*. (*Patna B.Sc. 1959*)

Ans. (*X*) C_2H_5CN (*Y*) C_2H_5COOH.

17. A neutral compound containing 25.5% nitrogen after being heated with dil. HCl gave an acid containing C, 48.7 & H, 8.1% but no nitrogen, 0.2 gm. of this acid required for neutralization 27.0 c.c. of N/10 NaOH, the V.D. of ethyl ester=51. What is the neutral compound ? (*Rajasthan, B.Sc., 1953*)

Ans. CH_3CH_2CN.

CHAPTER TWENTY-EIGHT

ALKYL COMPOUNDS OF SULPHUR AND ARSENIC

1. General.—Sulphur follows oxygen in Group VI of the periodic table, and may, therefore, be expected to form alkyl compounds analogous to those of oxygen. Compounds containing alkyl radicals in union with sulphur are known, those derived from bicovalent sulphur being similar, in certain respects, to those containing oxygen. However, sulphur differs from oxygen in its capacity to become tetra- and hexacovalent.

2. Thio-alcohols, Thiols or Mercaptans, —RSH. These, as the name indicates, are alcohols in which the oxygen atom has been replaced by sulphur. They may also be regarded as derived from H_2S by the replacement of a hydrogen atom by an alkyl group, and, for that reason, are sometimes called **alkyl hydrosulphides.** The name "mercaptan" (L. *mercurium captans*, laying hold of mercury) refers to their power to form water-insoluble compounds with mercury and certain other metals, the hydrogen of the —SH group being replaced by the metal.

The I.U.C. names of thio-alcohols are derived from those of the parent hydrocarbons by adding the suffix *-thiol*. Thus, CH_3SH and C_2H_5SH are named methanethiol and ethanethiol respectively.

Methods of Formation.—

(1) Mercaptans may be obtained from *alkyl halides*, by distilling the latter with potassium hydrosulphide :

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + KSH \rightarrow \underset{\substack{\text{Ethyl mercaptan}\\\text{(Ethanethiol)}}}{C_2H_5SH} + KBr$$

(2) Alkyl halides may, with advantage, be replaced by *potassium alkyl sulphates* in the above reaction :

$$C_2H_5\boxed{KSO_4 + K}SH \rightarrow C_2H_5SH + K_2SO_4$$

This is to be preferred, since both the reactants are readily soluble in water and react in aqueous solution.

(3) Thio-alcohols may also be obtained from *alcohols* by the action of phosphorus pentasulphide,

$$5C_2H_5OH + P_2S_5 \rightarrow 5C_2H_5SH + P_2O_5$$

or by passing the alcohol vapour mixed with hydrogen sulphide over heated thoria :

$$C_2H_5OH + HSH \rightleftharpoons C_2H_5SH + HOH$$

The latter reaction is reversible, the yield in one passage over thoria at 360° being about 35 per cent with ethyl alcohol and about 45 per cent with methyl and propyl alcohols.

Physical Properties. Thio-alcohols are colourless liquids having an extremely nauseous smell. They are practically insoluble in water, and boil much lower than the corresponding alcohols. Thus, whereas methanol boils at 60°, methanethiol boils at 6°. Similarly, the boiling-points of the ethane compounds are 78° and 36° respectively.

Reactions. (1) *Oxidation.* Mercaptans are oxidized by atmospheric oxygen into **disulphides** ; *e.g.*,

$$\underset{\text{Ethyl mercaptan}}{2C_2H_5SH} + O \rightarrow \underset{\text{Ethyl disulphide}}{C_2H_5S.SC_2H_5} + H_2O$$

The reaction between a mercaptan and iodine,

$$2C_2H_5SH + I_2 \rightleftharpoons C_2H_5S.SC_2H_5 + 2HI,$$

is reversible. If, however, a considerable quantity of water be added, the hydriodic acid goes into the aqueous layer and the reaction proceeds to completion. This affords a method for the **quantitative estimation** of a mercaptan. An excess of a standard iodine solution is added to the sample to be analysed, and the iodine left over is titrated against standard sodium thiosulphate.

Nitric acid oxidizes thio-alcohols into **sulphonic acid :**

$$C_2H_5SH + 3O \rightarrow \underset{\text{Ethyl sulphonic acid}}{C_2H_5SO_2OH}$$

(2) *Formation of Mercaptides.* Thiols are much stronger acids than alcohols, and react with bases to form salts, called **mercaptides,** which are not much hydrolysed in aqueous solution,

$$C_2H_5SH + NaOH \rightleftharpoons \underset{\text{Sodium mercaptide}}{C_2H_5SNa} + H_2O$$

Mercury and many other heavy metals form insoluble mercaptides, *e.g.*,

$$2C_2H_5SH + HgO \rightarrow \underset{\text{Mercuric mercaptide}}{(C_2H_5S)_2Hg} + H_2O$$

The formation of water-insoluble mercaptides (especially those of mercury and silver) is utilized in the separation of mercaptans from mixtures. The mercaptides are readily decomposed by strong, dilute acids, with the production of original mercaptans ; *e.g.*,

$$(C_2H_5S)_2Hg + \underset{\text{(dilute)}}{H_2SO_4} \rightarrow 2C_2H_5SH + HgSO_4$$

The formation of water-soluble mercaptides is also utilized in the refining of petroleum, which often contains small amounts of thiols. These are undesirable because of their odour and the acidic nature of the products of combustion (SO_2 and SO_3).

(3) *Esterification.* Mercaptans resemble alcohols in their reaction with carboxylic acids, a **thioester** being produced and a molecule of water eliminated :

$$CH_3CO\boxed{OH + H}S{-}C_2H_5 \rightarrow \underset{\text{Ethyl thioacetate}}{CH_3C{\lessdot}^{O}_{SC_2H_5}} + H_2O$$

The fact that **water is eliminated**, and *not hydrogen sulphide*, is of considerable theoretical interest, and was formerly regarded as sufficient evidence that in the analogous reaction between an alcohol and a carboxylic acid, water is produced by the union between the *hydroxyl group of the acid* and the hydrogen atom of the alcohol. A *direct* proof of the origin of water during esterification of a carboxylic acid is given on page 199.

(4) *Reaction with Aldehydes and Ketones.* With aldehydes, mercaptans yield **thioacetals or mercaptals** and with ketones **thioketols or mercaptols**; *e.g.*,

$$CH_3CHO + 2HSC_2H_5 \rightarrow \underset{\text{Acetaldehyde mercaptal}}{CH_3CH{<}^{SC_2H_5}_{SC_2H_5}} + H_2O$$

$$^{CH_3}_{CH_3}{>}CO + 2HSC_2H_5 \rightarrow \underset{\text{Acetone mercaptol}}{^{CH_3}_{CH_3}{>}C{<}^{SC_2H_5}_{SC_2H_5}} + H_2O$$

3. Ethyl Mercaptan. C_2H_5SH.—Ethyl mercaptan, commonly known as **mercaptan**, is the most important of the thioalcohols. It is prepared on a commercial scale by the interaction of ethyl chloride and potassium hydrosulphide. It is a particularly offensive smelling liquid, b.p., 36°. Its reactions have already been discussed.

Uses. (1) The chief use of mercaptan is in the manufacture of *sulphonal*.

(2) Mercaptan is also used for imparting an odour to illuminating gas and refrigerating fluids. Should a leakage occur, the odour serves to give the necessary warning.

4. Sulphonal, *Acetone-diethylsulphone*, $^{CH_3}_{CH_3}{>}C{<}^{SO_2C_2H_5}_{SO_2C_2H_5}$.

This important sleep-inducing drug is manufactured from acetone and ethyl mercaptan, which, as already mentioned, condense together to form acetone mercaptol :—

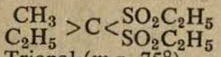
$$\underset{\text{Acetone}}{^{CH_3}_{CH_3}{>}CO} + 2HSC_2H_5 \rightarrow \underset{\text{Acetone mercaptol}}{^{CH_3}_{CH_3}{>}C{<}^{SC_2H_5}_{SC_2H_5}} + H_2O$$

The latter on oxidation with potassium permanganate gives sulphonal :—

$$\underset{\text{Acetone mercaptol}}{^{CH_3}_{CH_3}{>}C{<}^{SC_2H_5}_{SC_2H_5}} + 4O \rightarrow \underset{\substack{\text{Acetone-diethylsulphone} \\ (\textit{sulphonal})}}{^{CH_3}_{CH_3}{>}C{<}^{SO_2C_2H_5}_{SO_2C_2H_5}}$$

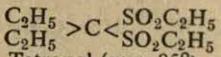
Sulphonal crystallizes in colourless prisms (*m.p.*, 126°), and is sparingly soluble in water. It is used in medicine as a hypnotic.

Sulphonal contains two ethyl groups in the molecule. The corresponding compounds containing 3 and 4 ethyl groups are called **trional** and **tetronal** respectively :



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$$

Trional (*m.p.* 75°)

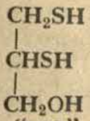


$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$$

Tetronal (*m.p.* 85°)

They are prepared in a corresponding manner to sulphonal, and like the latter, are useful hypnotics.

5. **"BAL"** (British anti-lewisite), *1-Propanol-2, 3-dithiol.* This compound was found by British chemists during World War II to be a very efficient antidote in arsenic poisoning arising from such war gases as Lewisite (p. 441). It combines with lewisite, etc., to form stable non-toxic compounds.



$$\begin{matrix}CH_2SH\\|\\CHSH\\|\\CH_2OH\end{matrix}$$

"BAL"

6. **Thio-Ethers** or *Dialkyl Sulphides.*—These compounds are prepared by the following methods :

(1) By distilling alkyl halides (or potassiumalkyl sulphates) with potassium sulphide :

$$2C_2H_5I + K_2S \rightarrow \underset{\text{Ethyl thio-ether}}{(C_2H_5)_2S} + 2KI$$

$$2C_2H_5KSO_4 + K_2S \rightarrow \underset{\text{Ethyl thio-ether}}{(C_2H_5)_2S} + K_2SO_4$$

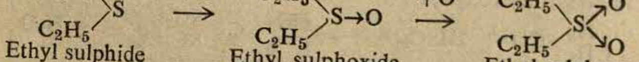
(2) By heating ether with phosphorus pentasulphide :

$$5(C_2H_5)_2O + P_2S_5 \rightarrow 5(C_2H_5)_2S + P_2O_5$$

Thio-ethers are neutral, volatile liquids having a disgusting odour.

Reactions. Thio-ethers do not contain hydrogen displaceable by metals, nor do they react with acid chlorides. Their chief reactions are due to the sulphur assuming a higher covalency.

(1) *Oxidation.* With mild oxidizing agents, thio-ethers take up one atom of oxygen, yielding **sulphoxides** ; on more vigorous oxidation, two atoms of oxygen are added, with the formation of **sulphones.** The first stage of the oxidation is best effected by means of hydrogen peroxide in acetic acid solution at room temperature and the second by heating with hydrogen peroxide or, better, by refluxing with permanganate :

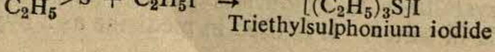


Ethyl sulphide Ethyl sulphoxide Ethyl sulphone

(2) *Addition of Halogens.* Thio-ethers directly combine with a molecule of halogen, forming dihalides ; *e.g.*,

$$(C_2H_5)_2S + Br_2 \rightarrow \underset{\text{Ethyl-thio-ether dibromide}}{(C_2H_5)_2SBr_2}$$

(3) *Addition of Alkyl Halides.* They also combine with alkyl halides as shown below :



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>S + C_2H_5I \rightarrow [(C_2H_5)_3S]I$$

Triethylsulphonium iodide

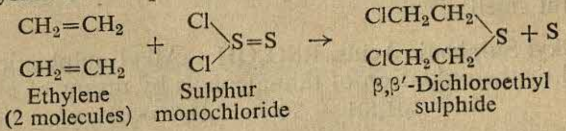
The resulting compounds are analogous to alkyl ammonium halides, and, when treated with silver hydroxide in aqueous solution, undergo double decomposition, yielding the strongly basic **trialkyl sulphonium hydroxides,** $[R_3S]OH$, which may be obtained as deliquescent oils by the evaporation of the solution.

(4) *Addition Compounds with Salts.* Thio-ethers form crystalline addition compounds with a large variety of salts, particularly with those of the heavy metals ; *e.g.*,

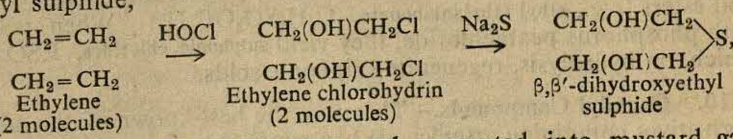
$$(C_2H_5)_2S,HgCl_2 \text{ and } [(C_2H_5)_2S]_2, SnCl_4.$$

Some of these addition compounds have definite melting points.

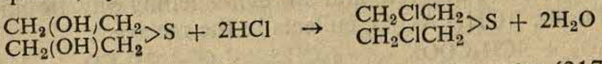
7. **Mustard Gas**[1], β, β′-*Dichloroethyl Sulphide.* This was the most destructive[2] gas used in Great War I. The English prepared it by passing ethylene into sulphur monochloride :



Another method, which gives a purer product not easily detectable, consists in preparing a non-poisonous intermediate, β, β′-dihydroxyethyl sulphide,



that can be handled with safety and converted into mustard gas, when required, by treatment with dry HCl gas :—



$$\begin{matrix}CH_2(OH)CH_2\\CH_2(OH)CH_2\end{matrix}{>}S + 2HCl \rightarrow \begin{matrix}CH_2ClCH_2\\CH_2ClCH_2\end{matrix}{>}S + 2H_2O$$

'Mustard gas' is, in reality, a **liquid of high boiling-point** (217°). It is sparingly soluble in, and heavier than, water (sp. gr. 1.28). Hence, though readily hydrolysed, if *shaken* with water, it may be kept under that liquid for a long time without much action.

Mustard gas has the **dual character of a double alkyl halide and a thio-ether.** Its chlorine atoms are immensely more reactive than those of ethyl chloride, and, even when shaken with water, the compound gets hydrolysed in a few minutes ; with alkalis, of course, the reaction is more rapid. As an alkyl sulphide, it is oxidized in two stages :

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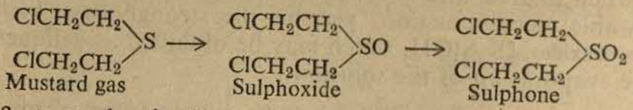
[1] The name 'mustard gas' was given to this substance from resemblance of its odour to that of mustard.

[2] The physiological action of mustard gas is very destructive. Its vapour produces bad burns on the skin. When inhaled, the effects are extremely serious though very delayed. Even when fatal concentrations are breathed, no inconvenience is felt for some hours. While of those killed by phosgene, over 80 per cent died within 24 hours, most of the mustard gas victims died on or after the fourth day.



$$(ClCH_2CH_2)_2S \longrightarrow (ClCH_2CH_2)_2SO \longrightarrow (ClCH_2CH_2)_2SO_2$$

Chlorine first attaches itself to the sulphur atom and then replaces one or more hydrogen atoms, the products being entirely non-toxic. Hence, the **best method of destroying mustard gas is by chlorination.**

8. Allyl Sulphide, $(CH_2=CHCH_2)_2S$.—This compound is the principal constituent of *oil of garlic* (*Allium sativum*), which may be obtained by distilling the macerated plant with water. Synthetically, it is prepared by distilling allyl iodide with potassium sulphide.

Allyl sulphide is a colourless liquid, b.p. 140°, and has a very unpleasant smell.

9. Alkyl Sulphonic Acids, RSO_2OH.—Alkyl sulphonic acids are obtained by the oxidation of thio-alcohols by means of nitric acid :

$$C_2H_5SH + 3O \rightarrow C_2H_5SO_2OH$$

They are extremely hygroscopic, crystalline substances, very readily soluble in water. Sulphonic acids are strongly acidic in character, and form metallic salts (*e.g.*, **potassium ethylsulphonate**, $C_2H_5SO_2OK$) and esters (*e.g.*, **ethyl ethylsulphonate**, $C_2H_5SO_2OC_2H_5$). When teated with phosphorus pentachloride, they yield **sulphonic chlorides**, RSO_2Cl, which, on hydrolysis, regenerate sulphonic acids.

10. Cacodyl Compounds.—These are the best-known of the alkyl derivatives containing arsenic. When equal quantities of arsenious oxide and potassium acetate are submitted to dry-distillation, highly poisonous gases are evolved, and an evil-smelling oily liquid, known at **cacodyl oxide**, $[(CH_3)_2As]_2O$, collects in the receiver :

$$As_2O_3 + 4CH_3COOK \longrightarrow [(CH_3)_2As]_2O + 2K_2CO_3 + 2CO_2$$

The composition of cacodyl oxide was found by Bunsen, who is also responsible for the name "**cacodyl**" (Gk. *kakodes*, stinking), which he gave to the **monovalent dimethylarsine group**, $(CH_3)_2As$—. The cacodyl group enters into the composition of a number of derivatives and is sometimes symbolized as Kd.

Cacodyl oxide boils at 120°, and, in the pure condition, is not spontaneously inflammable.[1] It is insoluble in water, and has a neutral reaction, but it dissolves in acids, forming salts, such as **cacodyl chloride**, $(CH_3)_2AsCl$.

When cacodyl chloride is heated with zinc in an atmosphere of carbon dioxide, it yields **cacodyl**, or **dicacodyl**, $(CH_3)_2As.As(CH_3)_2$. This substance, like cacodyl oxide, is an exceedingly poisonous, evil-smelling liquid, and is spontaneously inflammable in air.

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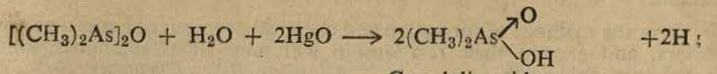
[1] The liquid prepared by the above-mentioned reaction is spontaneously inflammable because of the presence of cacodyl.

When cacodyl oxide is oxidized by means of mercuric oxide, it yields **cacodylic acid** :



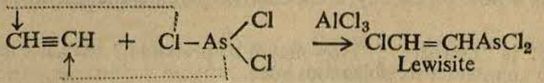
$$[(CH_3)_2As]_2O + H_2O + 2HgO \longrightarrow 2(CH_3)_2As\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} \quad +2H;$$

Cacodylic acid

This is a crystalline, inodorous substance, and seems to be non-poisonous. Certain metallic salts of this acid, *e.g.*, sodium, calcium, and mercury cacodylates, are used in the treatment of syphilis, malaria and pellagra.[1]

The formation of cacodyl oxide constitutes a **delicate test for acetates.** It should, however, be remembered that the compound is exceedingly poisonous. Hence, only **minute quantities** of the reactants should be used and the amount of the vapour inhaled should be absolutely minimum.

11. Lewisite (**β-Chlorovinyldichloroarsine**).—This is a war "gas" developed by W. L. Lewis, an American chemist, in 1917. The method of manufacture consists in the addition of arsenic trichloride to acetylene in the presence of anhydrous aluminium chloride (catalyst):



$$CH{\equiv}CH + Cl{-}As\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} \xrightarrow{AlCl_3} ClCH{=}CHAsCl_2$$

Lewisite

It is interesting to note that lewisite has never been used so far. The first lot, released in November, 1918, was destroyed at sea, following the declaration of Armistice (World War I).

Lewisite combines a vesicant action like that of mustard gas with the poisoning effect of arsenic, and produces immediate casualties. It is about four times as quick-acting as mustard gas. The breathing of air that contains 0.048 mg. of it per litre causes death in half an hour.

The best antidote for Lewisite is "BAL" (p. 438).

QUESTIONS

1. How are thio-alcohols and thio-ethers prepared ? Illustrate the statement that the chemical behaviour of the compounds is due to the tendency of bivalent sulphur to pass to the tetravalent state. (*Patna, B.Sc., 1952*)

2. How are mercaptans prepared? Give their physical and chemical properties. Describe the preparation of sulphonal, and mention its uses. (*Nagpur, B.Sc., 1952*)

3. How would you prepare sulphonal and what are its chief chemical properties ? (*Punjab, B Sc., 1950*)

4. How would you proceed to synthesise (*a*) Sulphonal, (*b*) Mustard gas ? (*Nagpur, B.Sc., 1953*)

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[1] A deadly, deficiency disease characterized by shrivelled skin and wasted body; often ending in insanity.

5. 0·205 gm. of a sample of commercial ethyl mercaptan required for complete oxidation 31.5 ml. of N/10 iodine solution. Calculate the percentage purity of the sample. (*Ans.* 95.3%)

6. Give the methods of formation and chemical properties of mercaptans and thioethers, and explain their relationship with sulphoxides, sulphones, sulphinic acids and sulphonic acids. (*Bombay, B.Sc., Chemistry, Subs., 1962*)

7. Give at least two methods for the preparation of ethyl mercaptan. (*Patna, B.Sc., 1959*)

8. Describe the preparation and reactions of ethyl mercaptan. (*Madras, B.Sc., 1953*)

9. How is ethyl mercaptan prepared ? (*Allahabad, B.Sc., 1951*)

10. How are thioalcohols and thioethers prepared ? Illustrate the statement that the chemical behaviour of the compounds is due to the tendency of divalent sulphur to pass into the tetravalent state. (*Punjab, B.Sc., 1952*)

11. (*a*) What are thio-alcohols, and how are they generally prepared ?
  (*b*) What is the action of the following on thio-ethyl alcohol ?
    (*i*) Mercuric chloride, and (*ii*) Strong Nitric acid ?
(*Karnatak B.Sc., 1960*)

12. Describe general methods of preparation of thioalcohols and thio-ethers.

How does nitric acid and hydrogen peroxide respectively react with : (*a*) ethyl mercaptan and (*b*) diethyl sulphide ?

Give the synthesis of sulphonal and mustard gas. (*Gujarat, B.Sc., 1960*)

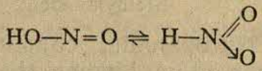
13. Write a note on cacodyl compounds. What is the 'cacodyl oxide test' for acetates ?

14. What is 'Lewisite' ? How may it be prepared ? What substance may be employed to counteract its poisonous effect ?

CHAPTER TWENTY-NINE

NITROPARAFFINS AND ALKYL NITRITES

1. Nitro Compounds. Nitrous acid gives rise to two series of isomeric alkyl derivatives, corresponding to its tautomeric forms :



$$HO—N=O \rightleftharpoons H—N\begin{matrix} \nearrow O \\ \searrow O \end{matrix}$$

The derivatives corresponding to the first form are called **alkyl nitrites** and those corresponding to the second form, **nitro compounds.** Alkyl nitrites (chap. 15, sec. 8, page 255) are obtained by the action of sodium nitrite and dilute sulphuric acid on alcohols, and possess the typical properties of an ester.

The nitro-compounds derived from paraffin hydrocarbons are called **nitroalkanes** or **nitroparaffins** and those derived from olefin hydrocarbons are named **nitro-olefins.**

2. Preparation of Nitroparaffins.—(1) Nitroparaffins are usually obtained by heating alkyl halides with silver nitrite :—

$$\underset{\text{Methyl iodide}}{CH_3I} + AgNO_2 \longrightarrow \underset{\text{Nitromethane}}{CH_3NO_2} + AgI$$

No methyl nitrite is produced in this reaction, but in the case of higher members an increasing proportion of alkyl nitrite accompanies the nitroparaffin. The mixture can, however, be readily separated by fractional distillation, as nitroparaffins boil much higher than the isomeric alkyl nitrites.[1]

(2) Nitroparaffins are often prepared from the corresponding α-halogen substituted acids. The latter, when treated with sodium nitrite, yield α-nitro-substituted acids, which readily lose carbon dioxide, giving nitroparaffins; *e.g.*,

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow{NaNO_2} \underset{\text{Nitroacetic acid}}{CH_2(NO_2)COOH} \xrightarrow{-CO_2} \underset{\text{Nitromethane}}{CH_3NO_2}$$

(3) Higher nitroparaffins can be prepared by the direct action of nitric acid on the hydrocarbons:

$$R\boxed{H + HO}NO_2 \longrightarrow RNO_2 + H_2O$$

The nitration is effected by heating, at about 110°, a mixture of the hydrocarbon with dilute nitric acid in a sealed tube for several hours.

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[1] Thus, while ethyl nitrite boils at 16°, nitro-ethane boils at 115°.

3. **Physical Properties.**—Nitroparaffins are colourless, pleasant-smelling liquids. They boil much higher than the isomeric nitrites. The lower members are slightly soluble in water, the solubility decreasing with the length of the carbon chain.

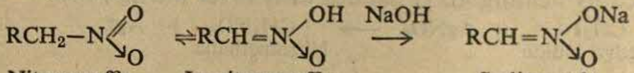
4. **Chemical Properties.**—

(1) **Reduction.** On reduction with tin and hydrochloric acid, and other reducing agents, nitroparaffins yield primary amines; *e.g.*,

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6H \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

(2) **Pseudo-acid character.** Nitroparaffins containing hydrogen in direct union with the carbon atom binding the nitro-group (*i.e.*, primary and secondary nitro-compounds, but *not* the tertiary) gradually dissolve in alkalis, yielding derivatives in which one of the hydrogen atoms of the nitro-compound is replaced by an atom of the alkali metal. The sodium compound is most readily obtained as a crystalline precipitate by mixing the nitro-compound in absolute alcoholic solution with sodium ethoxide or methoxide. The insolubility of the sodium salts in absolute alcohol may be employed for the **separation of nitroparaffins** from other compounds.

The alkali salts are not derived from nitroparaffins but from labile isomerides, called **isonitroparaffins.** Thus:



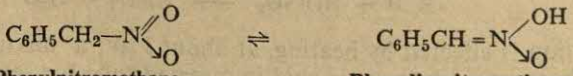
$$RCH_2{-}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O} \rightleftharpoons RCH{=}N\genfrac{}{}{0pt}{}{\nearrow OH}{\searrow O} \xrightarrow{NaOH} RCH{=}N\genfrac{}{}{0pt}{}{\nearrow ONa}{\searrow O}$$

Nitroparaffin Isonitroparaffin Sodium salt

Nitroparaffins, therefore, are tautomeric substances. The isonitro form, being a true acid, is called the **aci-form**, while the true nitro-compound, which is neutral in character, is termed a **pseudo-acid.**

When the solution of the alkali salt of a nitroparaffin is acidified, the *aci*-nitroparaffin, first set free, rapidly changes into the stable nitroparaffin.

From **phenylnitromethane**, $C_6H_5CH_2NO_2$, Hantzsch (1896) was able to isolate both the isomeric forms. The true nitro-form is a neutral, oily liquid (*b.p.* 227°), having no power to conduct the electric current. By carefully decomposing the sodium derivative with an acid, the isonitro-form is obtained as a colourless solid (*m.p.*, 82°), which is found to be a conductor of electricity, and even in the solid state slowly changes into the oily nitro-form.



$$C_6H_5CH_2{-}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O} \rightleftharpoons C_6H_5CH{=}N\genfrac{}{}{0pt}{}{\nearrow OH}{\searrow O}$$

Phenylnitromethane
(Nitro-form; neutral oily liquid; stable when heated; gives no immediate reaction with $FeCl_3$; dissolves in alkalis *very slowly*)

Phenylisonitromethane
(Aci-form; colourless crystals; gives *immediate* red colour with $FeCl_3$; *quickly* dissolves in alkalis; passes into normal form on heating or standing)

(3) **Bromination.** When an alkaline solution of a nitroparaffin is treated with *bromine*, the hydrogen atoms (if any) linked to the carbon atom binding the nitro-group are replaced by bromine. Thus nitroethane, $CH_3CH_2NO_2$, yields monobromo- and dibromo- derivatives, $CH_3CHBrNO_2$, and $CH_3CBr_2NO_2$. The former has the properties of a pseudo-acid, while the latter is a neutral substance insoluble in alkalis.

(4) **Action of Nitrous Acid.** The action of *nitrous acid* on primary and secondary nitroparaffins has already been described (p. 235).

5. Distinctive Properties of Nitroparaffins and Alkyl Nitrites.—

(1) As already mentioned, nitroparaffins boil at much higher temperatures than their isomeric alkyl nitrites.

(2) Alkyl nitrites, like other esters, are readily hydrolysed by alkalis, yielding alkali metal nitrites and the corresponding alcohols :

$$C_2H_5NO_2 + NaOH \longrightarrow C_2H_5OH + NaNO_2$$

Nitroparaffins are not decomposed by alkalis, but, as already stated, they slowly dissolve in alkali solutions, forming metallic salts.

(3) Upon reduction with tin and hydrochloric acid, and other strong reducing agents, nitroparaffins yield the corresponding primary amines; *e.g.*,

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6H \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

Alkyl nitrites, under the same conditions, undergo hydrolysis, accompanied by reduction of the resulting nitrous acid to ammonia or hydroxylamine; *e.g.*,

$$\begin{array}{c} C_2H_5NO_2 + HOH \longrightarrow C_2H_5OH + HNO_2 \\ \underline{HNO_2 + 6H \longrightarrow NH_3 + 2H_2O} \\ C_2H_5NO_2 + 6H \longrightarrow C_2H_5OH + NH_3 + H_2O \end{array}$$

(4) Primary and secondary nitro-paraffins react with nitrous acid, yielding nitrolic acids and pseudo-nitrols respectively (p. 235). Alkyl nitrites do not react with nitrous acid.

QUESTIONS

1. Give the preparation and chief properties of *nitroparaffins*. What other alkyl derivatives of nitrous acid are known, and in what respects do they differ from nitroparaffins ? *(Punjab, B.Sc., 1943)*

2. Write a note on Nitroparaffins.

3. Write an account of the aliphatic nitro-compounds. *(Ceylon, B.Sc., 1953)*

4. How will you distinguish between Ethyl nitrite and Nitroethane ? Explain the reactions with equations. *(Nagpur, B.Sc., 1953)*

5. Describe the preparation and chief properties of nitroparaffins. What other alkyl derivatives of nitrous acid are known and in what respects do they differ from nitroparaffins ? *(Andhra, B.Sc., 1955)*

6. What are the nitroparaffins ? How are they obtained ? How do they differ from the alkyl nitrites ? How are nitroparaffins used for distinguishing between the primary, secondary and the tertiary alcohols ? *(Nagpur, B.Sc., 1960)*

7. Discuss the isomerism of alkyl nitrites and nitroparaffins. (*Agra, B.Sc., 1959*)

8. How would you prepare nitroethane ? Explain how it differs from ethyl nitrite in properties and molecular structure. (*Agra, B.Sc., 1957*)

9. An organic compound gave the following results : C, 32.0% ; H, 6.66%, N, 18.67% ; Molecular Weight, 75.

(*i*) On hydrolysis it gave an alcohol *B*, mol. wt. = 46, together with an acid.

(*ii*) On reduction it gave the same alcohol *B*, but together with NH_3. What is the formula of *A* ? (*Agra, B.Sc., 1959*)

Ans. Ethyl nitrite, $C_2H_5NO_2$.

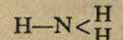
10. An organic compound *A* contains C=32%, H=6.66% and N=18.67%. On reduction it gave a primary amine *B* which gave ethyl alcohol with nitrous acid. *B* gave an offensive odour on warming with chloroform and KOH and forming another compound *C* which on reduction gave methylethylamine. What formulae would you assign to A, B and C ? Explain these reactions. (*Rajasthan, B.Sc., 1958*)

Ans. (*A*) Nitroethane, $C_2H_5NO_2$ (*B*) Ethylamine, $C_2H_5NH_2$ (*C*) Ethyl isocyanide, C_2H_5NC.

CHAPTER THIRTY

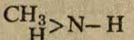
AMINES AND QUATERNARY AMMONIUM DERIVATIVES

1. General.—Amines are derived from ammonia by the replacement of hydrogen atoms by alkyl groups. They are termed *primary*, *secondary* or *tertiary*, according as one, two or three hydrogen atoms have been thus replaced :



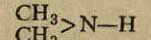
$H{-}N<^{H}_{H}$

Ammonia



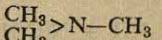
$^{CH_3}_{H}{>}N{-}H$

Methylamine (primary amine)



$^{CH_3}_{CH_3}{>}N{-}H$

Dimethylamine (secondary amine)



$^{CH_3}_{CH_3}{>}N{-}CH_3$.

Trimethylamine (tertiary amine)

In all the three classes of amines, as in ammonia itself, the nitrogen atom is tricovalent. Tertiary amines combine with alkyl halides to form quaternary ammonium salts :

$$R_3N + RI \rightarrow R_4NI,$$

which, on treatment with silver hydroxide, yield **quaternary ammonium hydroxides**, R_4NOH. These latter compounds are of strongly basic character, being nearly as strong as alkali hydroxides.

The alkyl groups in a secondary or a tertiary amine may be alike or they may be different. In the former case, the amine is said to be *simple*, and in the latter, *mixed* (compare ethers).

I.U.C. Nomenclature.—

In the I.U.C. system, primary, secondary and tertiary amines are named **aminoalkanes**, **alkylaminoalkanes** and **dialkylaminoalkanes** respectively. The following table gives the I.U.C. and the common names of a few amines, side by side :

Formula	Common Name	I.U.C. name
$CH_3CH_2CH_2NH_2$	*n*-Propylamine	1-Aminopropane
$CH_3CH(NH_2)CH_3$	Isopropylamine	2-Aminopropane
$CH_3CH(NHCH_3)CH_3$	Methylisopropylamine	2-Methylaminopropane
$CH_3\underset{\underset{N(CH_2CH_3)_2}{\vert}}{C}HCH_2CH_3$	Diethyl-*sec*-butylamine	2-Diethylaminobutane

2. Preparation of Primary, Secondary and Tertiary Amines by ✓ Alkylation of Ammonia.

(1) *Alkylation by means of Alkyl Halides.*—**Hofmann's method** (1849). Hofmann discovered that when an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of the salts derived from primary, secondary and tertiary amines and a quaternary ammonium salt is formed. Thus, with ethyl iodide the reaction occurs in the following stages, which proceed *simultaneously*.

$$(i)\ C_2H_5\boxed{I + H}NH_2 \rightarrow \underset{\text{Ethylamine hydriodide}^1}{C_2H_5NH_2.HI}$$

$$(ii)\ C_2H_5\boxed{I + H}NH(C_2H_5) \rightarrow \underset{\text{Diethylamine hydriodide}}{(C_2H_5)_2NH.HI}$$

$$(iii)\ C_2H_5\boxed{I + H}N(C_2H_5)_2 \rightarrow \underset{\text{Triethylamine hydriodide}}{(C_2H_5)_3N.HI}$$

$$(iv)\ C_2H_5I + N(C_2H_5)_3 \rightarrow \underset{\text{Tetraethylammonium iodide}}{[(C_2H_5)_4N]I}$$

In the laboratory, alkyl *iodides* are used because of the comparative ease with which they can be manipulated. On the technical scale, on the other hand, the cheaper alkyl *bromides* are preferred.

(2) *Catalytic Alkylation.* Sabatier and Mailhe discovered (1900) that when the vapour of an alcohol mixed with ammonia is led over certain oxides at 360°, a mixture of primary, secondary and tertiary amines is formed :

$$C_2H_5\boxed{OH + H}NH_2 \longrightarrow C_2H_5NH_2 + H_2O$$

$$C_2H_5\boxed{OH + H}HNC_2H_5 \longrightarrow (C_2H_5)_2NH + H_2O$$

$$C_2H_5\boxed{OH + H}N(C_2H_5)_2 \longrightarrow (C_2H_5)_3N + H_2O$$

Alumina, thoria, blue oxide of tungsten, and silica gel have been found to be good catalysts for this reaction.

(3) *Methylation with Dimethyl Sulphate.* Ullman found (1900) dimethyl sulphate to be a suitable methylating agent for primary and secondary amines :

$$\underset{\text{Methylamine}}{CH_3NH_2} + (CH_3)_2SO_4 \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + CH_3HSO_4$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + (CH_3)_2SO_4 \longrightarrow \underset{\text{Methylethylamine}}{C_2H_5NHCH_3} + CH_3HSO_4$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} + (CH_3)_2SO_4 \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3HSO_4$$

(4) *Methylation with Formaldehyde.* A very convenient method of methylating ammonia and primary and secondary amines is by means of formaldehyde. The amine or ammonia in *acid solution* is heated with a 40 per cent aqueous solution of formaldehyde, when methylation occurs as shown below :—

$$\begin{array}{ll} 3HCHO + H_2O \longrightarrow 2CH_3OH + CO_2 & \\ \underline{NH_3 + CH_3OH \longrightarrow CH_3NH_2 + H_2O} & [\times 2] \\ 2NH_3 + 3HCHO \longrightarrow 2CH_3NH_2 + CO_2 + H_2O & \end{array}$$

Thus we see that **three molecules of formaldehyde are required for the**

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[1] More correctly *Monoethylammonium iodide*, $C_2H_5NH_3I$.

displacement of two hydrogen atoms by methyl groups. Prolonged treatment with an excess of formaldehyde produces secondary and tertiary amines :

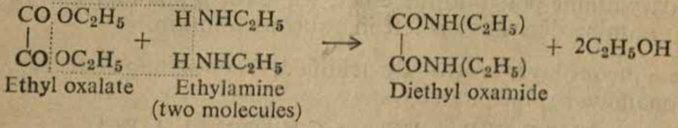
$$2CH_3NH_2 + 3HCHO \longrightarrow 2(CH_3)_2NH + CO_2 + H_2O$$
$$2(CH_3)_2NH + 3HCHO \longrightarrow 2(CH_3)_3N + CO_2 + H_2O$$

3. Separation of Primary, Secondary and Tertiary Amines.— In the preparation of amines by the alkylation of ammonia the same difficulties are met with as in the chlorination of methane. In both cases, mixtures are obtained that are difficult to separate. If the product contains a quaternary ammonium salt, in addition to the amines (as in Hofmann's method), it is distilled with potassium hydroxide. The mixture of amines passes over, while the quaternary ammonium salt, being not decomposed by alkali, is left behind.

The mixture of primary, secondary, and tertiary amines may be separated by one of the following methods :—

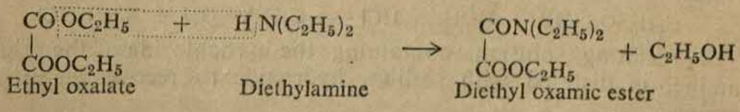
(1) *Physical Methods.* The ethylamines and the higher members can be best separated by **fractional distillation** through effective columns. The lower members, methylamines and ethylamines may be separated by *fractional crystallization* of their hydrochlorides.

(2) *With Ethyl Oxalate* (**Hofmann's Method**). In this method, the mixture of primary, secondary and tertiary amines is treated with ethyl oxalate. The primary amines give a **dialkyl oxamide** which is a colourless crystalline solid, soluble in hot water :



$$\underset{\text{Ethyl oxalate}}{\begin{array}{l}\mathrm{CO\,OC_2H_5}\\ |\\ \mathrm{CO\,OC_2H_5}\end{array}} + \underset{\substack{\text{Ethylamine}\\ \text{(two molecules)}}}{\begin{array}{l}\mathrm{H\,NHC_2H_5}\\ \\ \mathrm{H\,NHC_2H_5}\end{array}} \longrightarrow \underset{\text{Diethyl oxamide}}{\begin{array}{l}\mathrm{CONH(C_2H_5)}\\ |\\ \mathrm{CONH(C_2H_5)}\end{array}} + 2C_2H_5OH$$

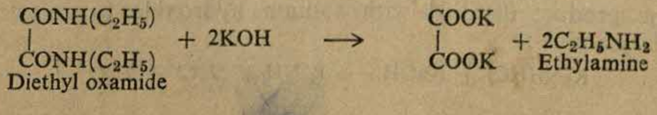
The secondary amine forms a **dialkyl oxamic ester**, a colourless liquid insoluble in water :



$$\underset{\text{Ethyl oxalate}}{\begin{array}{l}\mathrm{CO\,OC_2H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array}} + \underset{\text{Diethylamine}}{\mathrm{H\,N(C_2H_5)_2}} \longrightarrow \underset{\text{Diethyl oxamic ester}}{\begin{array}{l}\mathrm{CON(C_2H_5)_2}\\ |\\ \mathrm{COOC_2H_5}\end{array}} + C_2H_5OH$$

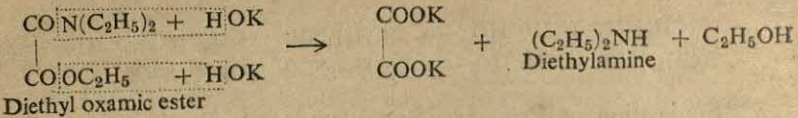
The tertiary amine does not react with ethyloxalate.

The reaction mixure is distilled, when tertiary amine passes over unchanged. The residue in the flask is extracted with hot water which removes the dialkyl oxamide. The aqueous solution of the amide, after being separated from the insoluble ester, is distilled with an excess of alkali, when the primary amine distils over :



$$\underset{\text{Diethyl oxamide}}{\begin{array}{l}\mathrm{CONH(C_2H_5)}\\ |\\ \mathrm{CONH(C_2H_5)}\end{array}} + 2KOH \longrightarrow \begin{array}{l}\mathrm{COOK}\\ |\\ \mathrm{COOK}\end{array} + \underset{\text{Ethylamine}}{2C_2H_5NH_2}$$

The insoluble dialkyl oxamic ester is separately distilled with alkali, when the secondary amine distils (together with ethyl alcohol) :



$$\begin{array}{l} CO\,N(C_2H_5)_2 + H\,OK \\ | \\ CO\,OC_2H_5 \quad + H\,OK \\ \text{Diethyl oxamic ester} \end{array} \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \end{array} + \underset{\text{Diethylamine}}{(C_2H_5)_2NH} + C_2H_5OH$$

(3) *With Benzenesulphonic Chloride* (**Hinsberg's Method**). This is a general method for effecting the separation of a mixture of primary, secondary and tertiary amines. The mixure is treated with *benzenesulphonic chloride*, $C_6H_5SO_2Cl$, when the primary and the secondary amines react, forming mono- and dialkyl derivatives of benzenesulphonamide, $C_6H_5SO_2NH_2$, while the tertiary amine is left unaffected :

$$C_6H_5SO_2Cl + \underset{\substack{\text{Primary}\\ \text{amine}}}{NH_2R} \longrightarrow \underset{\substack{\text{Monalkyl benzene-}\\ \text{sulphonamide}}}{C_6H_5SO_2NHR} + HCl$$

$$C_6H_5SO_2Cl + \underset{\substack{\text{Secondary}\\ \text{amine}}}{NHR_2} \longrightarrow \underset{\substack{\text{Dialkyl benzene-}\\ \text{sulphonamide}}}{C_6H_5SO_2NR_2} + HCl$$

The monalkyl derivative, because of the hydrogen atom linked to nitrogen being replaceable by metals, is soluble in KOH, forming the potassium salt, $C_6H_5SO_2NKR$. The dialkyl derivative, since it contains no such hydrogen atom, is insoluble in KOH. The reaction mixture is, therefore, strongly alkalified with KOH, and then extracted with ether. The tertiary amine and the derivative of the secondary amine pass into the ether, while the potassium salt of the primary amine derivative is left in aqueous solution.

The aqueous layer is strongly acidified, when monoalkyl benzenesulphonamide is precipitated,

$$C_6H_5SO_2NKR + HCl \longrightarrow C_6H_5SO_2NHR + KCl,$$

which, after being separated, is hydrolysed by boiling with concentrated hydrochloric acid :

$$C_6H_5SO_2NHR + HOH + HCl \longrightarrow C_6H_5SO_2OH + RNH_2HCl$$

The resulting solution, containing the hyrochloride of the primary amine, is distilled with sodium hydroxide to recover the primary amine :

$$RNH_2HCl + NaOH \longrightarrow RNH_2 + NaCl + H_2O$$

The ethereal layer is subjected to fractional distillation, in order to separate the tertiary amine and the derivative of the secondary amine. The latter is then hydrolysed by boiling with concentrated hydrochloric acid,

$$C_6H_5SO_2NR_2 + HOH + HCl \longrightarrow C_6H_5SO_2OH + R_2NHHCl,$$

and the product distilled with sodium hydroxide to recover the secondary amine :

$$R_2NHHCl + NaOH \longrightarrow R_2NH + NaCl + H_2O$$

The various steps in Hinsberg's method ar

$$\left\{\begin{matrix} RNH_2 \\ R_2NH \\ R_3N \end{matrix}\right\} \xrightarrow{C_6H_5SO_2Cl} \left\{\begin{matrix} C_6H_5SO_2NH \\ C_6H_5SO_2NR \\ R_3N \end{matrix}\right.$$

Aqueous layer
($C_6H_5SO_2NKR$)
↓ Acidify
ppt.
($C_6H_5SO_2NHR$)
↓ Boil with conc. HCl
NH_2RHCl
↓ Distil with NaOH
RNH_2

$C_6H_5SO_2$
↓ E
R_2NHI
↓
R_2NH

(4) *By means of Nitrous Acid.* (Se

4. Preparation of Primary Amines secondary and tertiary) can be obtain

(1) *By Reduction of Nitriles* (**Mendiu** boiling the nitriles with sodium and a

$$\underset{\substack{\text{Methyl cyanide}\\\text{(acetonitrile)}}}{CH_3C{\equiv}N} + 4H \longrightarrow$$

(2) *By Reduction of Nitroparaffin* means of tin and hydrochloric acid:—

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6H \longrightarrow$$

(3) *By Hydrolysis of Alkyl Isocyan* brought about by treatment with dilu

$$\underset{\text{Methyl isocyanate}}{CH_3N{=}CO} + H_2O \longrightarrow$$

(4) *By Hydrolysis of alkyl Isocyani* of dilute acids:—

$$\underset{\text{Methyl isocyanide}}{CH_3NC} + 2H_2O \rightarrow \underset{\text{Methy}}{CH}$$

(5) **Hofmann's Bromamide Reaction.** primary amines, uncontaminated w good yields. The reaction has alr perties of Amides (chap. 21, sec. 12).

(6) **Gabriel's Phthalimide Reaction.** I when treated with alcoholic potash, $C_6H_4<^{CO}_{CO}>NK$. This, on treatm changes the potassium atom for an al

$$\underset{\text{Potassium phthalimide}}{C_6H_4<^{CO}_{CO}>NK} + RI \rightarrow$$

---

asses of aliphatic amines are solutions. This is due to their le corresponding **alkylammonium** I⁻ ions. Thus, in the case of

$$_3]OH \rightleftharpoons \underset{\text{Methylammonium ion}}{[CH_3NH_3]^+} + \underset{\text{Hydroxide ion}}{OH^-}$$

onium ne base)

s solution behave exactly like

form salts, such as methyl-

of heavy metals from aqueous

$$Fe(OH)_3 + 3(CH_3NH_3)Cl$$

s with cupric salts.

combine with auric chloride, and ites and chloroplatinates, such as $(C_2H_5NH_3)_2[PtCl_6]$.

nary aliphatic amines react with ols with evolution of nitrogen :

$$OH + N_2 + H_2O$$

ous acid, yielding **nitrosamines**:

$$R_2N.NO + H_2O$$

N yellowish-red, oils having an eat value in the **purification and** n a nitrosamine is warmed with c acid, the product poured into a deep blue or violet coloration **ion).** Nitrosamines are converted with concentrated hydrochloric

react with nitrous acid or are

ay also be utilized for the **separation** a mixture of the three classes of ed in an excess of concentrated rated solution of sodium nitrite is extracted with ether, purified, t with concentrated hydrochloric remains in the aqueous layer ered by distillation with caustic sent in the mixture is destroyed by

(3) **Alkylation.** Another method of distinguishing between the three classes of amines consists in the determination of the number of alkyl groups with which the amine can combine (compare alkylation of ammonia, sec. 2). The substance under examination is **heated with excess of methyl iodide**, when a quaternary ammonium iodide is obtained. By analysing the amine itself and the resulting quaternary ammonium iodide[1], we can determine the *number of methyl groups that have entered the molecule,* and thus classify the original amine. For example, a compound C_3H_9N is propylamine, $C_3H_7NH_2$, methylethylamine, $CH_3NHC_2H_5$, or trimethylamine, $(CH_3)_3N$, according as it gives $C_6H_{16}NI$, $C_5H_{14}NI$, or $C_4H_{12}NI$. (See foot-note).[2]

(4) **Acylation.** Like ammonia, primary and secondary amines react with acid chlorides, an acyl group being substituted for the replaceable hydrogen of the amine : *e g.,*

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + CH_3COCl \longrightarrow \underset{\text{N-Ethylacetamide}^3}{C_2H_5NHCOCH_3} + HCl$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} + CH_3COCl \longrightarrow \underset{\text{N-Dimethylacetamide}^3}{(CH_3)_2NCOCH_3} + HCl$$

Tertiary amines do not react.

In a primary amine, acetyl chloride usually replaces only one of the two hydrogen atoms linked to nitrogen, though in certain cases diacetylation may occur.

Acetyl derivatives of amines are crystalline solids of definite melting point, and are often used for the identification of the bases.

Benzenesulphonic chloride, $C_6H_5SO_2Cl$, as already mentioned, has been used by Hinsberg for distinguishing and isolating the three classes of amines from one another (sec. 3).

(5) **Carbylamine reaction for primary amines.** When a primary amine is warmed with chloroform and alcoholic potash, highly disgusting odour of an isocyanide or carbylamine, RNC, is developed.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

Secondary and tertiary amines do not give this reaction.

(6) **Fermentation of amines to produce alcohols.** Certain yeasts and moulds bring about the fermentation of primary amines as follows :—

$$RNH_2 + HOH \longrightarrow ROH + NH_3$$

The ammonia is converted into proteins by the yeast and assimilated, while alcohol remains in the fermented liquid.

(7) *Reaction with Grignard's Reagents.* (See page 217).

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[1] This is most readily done by titrating the iodion of the salt against standard $AgNO_3$.

[2] *i.e.,* $C_3H_7(CH_3)_3NI$, $C_2H_5(CH_3)_3NI$, or $(CH_3)_4NI$.

[3] The letter N here indicates that the alkyl group has replaced the hydrogen linked to the *nitrogen* atom of the acetamide molecule.

9. Ascent and Descent of Homologous Series.—Formation of a primary amine may be employed for the ascent or descent of a homologous series. In the former case, the additional carbon atom is introduced in the form of a —CN group, which may be reduced to the $—CH_2NH_2$ group by Mendius reaction. The resulting amine may then be converted into an alcohol by treatment with nitrous acid as in the following example :

$$\underset{\substack{\text{Methyl}\\\text{alcohol}}}{CH_3OH} \xrightarrow{HI} \underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} \xrightarrow{KCN} \underset{\substack{\text{Methyl}\\\text{cyanide}}}{CH_3CN} \xrightarrow{2H} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

The *descent* of a homologous series is effected through Hofmann's bromamide reaction as in the following example :—

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Ammonium acetate}}{CH_3COONH_4}$$

$$\xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methyl alcohol}}{CH_3OH}$$

10. Individual Amines.—

Methylamine, CH_3NH_2, occurs in *Mercurialis perennis*, and may be readily prepared by the interaction of ammonia and dimethyl sulphate or from acetamide by the bromamide reaction. It is produced largely by the decomposition of alkaloids and proteins. It is a colourless gas with an ammoniacal odour; it burns with a yellow flame, and is exceedingly soluble in water (1150 vols. in 1 vol. at 12·5°).

Dimethylamine, $(CH_3)_2NH$, is present in herring brine, being derived from the decomposition of the fishy material. It is most readily obtained by heating *p*-nitrosodimethylaniline with sodium hydroxide. It is a colourless liquid (*b.p.* 7°), and possesses an ammoniacal odour.

Trimethylamine, $(CH_3)_3N$, is also present in herring brine. It may be obtained pure by heating tetramethylammonium hydroxide (see below). On a commercial scale, it is prepared from beet molasses. It boils at 3·5°.

Ethylamines, $C_2H_5NH_2$, $(C_2H_5)_2NH$, and $(C_2H_5)_3N$, are liquids boiling at 19°, 56° and 90° respectively.

11. Tetramethylammonium Hydroxide.—$[(CH_3)_4N]OH$. This compound is obtained by the addition of silver hydroxide to *tetramethylammonium iodide :*

$$[(CH_3)_4N]I + AgOH \rightleftharpoons [(CH_3)_4N]OH + AgI$$

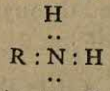
It is a colourless, deliquescent, crystalline substance, and is freely soluble in water, yielding a strongly alkaline solution, which absorbs carbon dioxide from the air. When heated, it decomposes into trimethylamine and methyl alcohol :

$$[(CH_3)_4N]OH \rightarrow (CH_3)_3N + CH_3OH$$

12. Higher Tetraalkylammonium Hydroxides.—Tetraethylammonium hydroxide and higher members closely resemble tetramethylammonium hydroxide, except that on heating they yield a tertiary amine, olefine, and water :

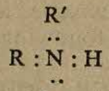
$$\underset{\text{Tetraethylammonium hydroxide}}{[(C_2H_5)_4N]OH} \rightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + \underset{\text{Ethylene}}{C_2H_4} + H_2O$$

13. Structure of Amines and Quaternary Ammonium Compounds.—Primary, secondary, and tertiary amines, being alkyl derivatives of ammonia, are assigned structures in which the nitrogen atom is tricovalent as shown below :—



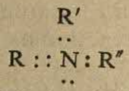
$$R:\underset{\cdot\cdot}{\overset{\overset{H}{\cdot\cdot}}{N}}:H$$

Primary amine



$$R:\underset{\cdot\cdot}{\overset{\overset{R'}{\cdot\cdot}}{N}}:H$$

Secondary amine



$$R::\underset{\cdot\cdot}{\overset{\overset{R'}{\cdot\cdot}}{N}}:R''$$

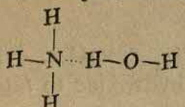
Tertiary amine

As is well known, ammonium hydroxide is a weak base, its strength being about the same as that of acetic acid. When its hydrogens are replaced by alkyl groups, the strength increases, but not to any great extent, until *all* the four have been replaced, the resulting tetra-alkyl ammonium hydroxides being almost as strong bases as potassium hydroxide. The following table summarizes the dissociation constants of methyl and ethyl ammonium bases :

DISSOCIATION CONSTANTS (×10,000) OF ETHYL AND METHYL AMMONIUM BASES AT 18°

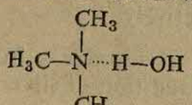
NH_4OH	0.30	——	
$N(CH_3)H_3OH$	4.9	$N(C_2H_5)H_3OH$	6.7
$N(CH_3)_2H_2OH$	14.2	$N(C_2H_5)_2H_2OH$	10.6
$N(CH_3)_3HOH$	0.7	$N(C_2H_5)_3HOH$	7.9
$N(CH_3)_4OH$	10,000	$N(C_2H_5)_4OH$	10,000

As is evident from the above table, the **introduction of the fourth alkyl group causes a sudden and enormous increase of strength**, which then becomes of quite another order. This striking transition from a weak to a strong base is explained by Sidgwick by assigning a covalent structure to ammonium hydroxide and its primary, secondary and tertiary derivatives and an electrovalent structure to quaternary ammonium bases as shown below :—



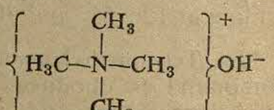
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\cdots H-O-H$$

Ammonium hydroxide



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}\cdots H-OH$$

Trimethylammonium hydroxide

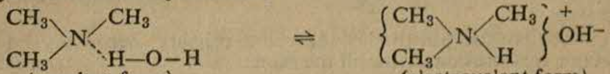


$$\left[H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^+OH^-$$

Tetramethylammonium hydroxide

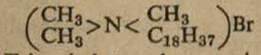
In the formulæ of ammonium hydroxide and its mono-, di- and trialkyl derivatives, the water molecule is supposed to be linked to the ammonia and amine molecule through a non ionizable hydrogen bond. As no such hydrogen atom is present in quaternary ammonium bases, there is no possibility of the formation of a hydrogen bond.

The slight ionization that the mono-, di- and trialkyl-ammonium hydroxide undergo is explained by the existence of an equilibrium between the covalent and electrovalent forms shown below for trimethylammonium hydroxide,


(covalent form) (electrovalent form)

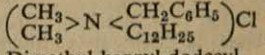
the equilibrium lying very largely to the left.

14. Higher Quaternary Ammonium Salts as Detergents.—As already mentioned, certain quaternary ammonium salts containing a long, normal alkyl radical (usually C_{12} to C_{18}), such as,


$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>N<\begin{matrix}CH_3\\C_{18}H_{37}\end{matrix}\right)Br$

Trimethyl-stearyl-ammonium bromide

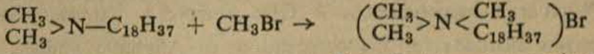
and


$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>N<\begin{matrix}CH_2C_6H_5\\C_{12}H_{25}\end{matrix}\right)Cl$

Dimethyl-benzyl-dodecyl-ammonium chloride

act as **cation active soaps**. They possess remarkable bactericidal properties, and are therefore used for sterilization of the skin, dishes and of various appliances in the food manufacturing industries.

They are prepared from tertiary amines having a long-chain alkyl group by the addition of an alkyl or aralkyl[1] chloride or bromide. Thus,


$$\begin{matrix}CH_3\\CH_3\end{matrix}>N-C_{18}H_{37} + CH_3Br \rightarrow \left(\begin{matrix}CH_3\\CH_3\end{matrix}>N<\begin{matrix}CH_3\\C_{18}H_{37}\end{matrix}\right)Br$$

Dimethylstearylamine Trimethylstearylammonium bromide

15. Amine Oxides.—When a tertiary amine is treated with hydrogen peroxide, it takes up an atom of oxygen, yielding an amine oxide ; *e.g.*,

$$(CH_3)_3N + H_2O_2 \rightarrow \underset{\text{Trimethylamine oxide}}{(CH_3)_3NO} + H_2O$$

The amine oxides crystallize from aqueous solution as hydrates (*e.g.*, $(CH_3)_3NO.2H_2O$; m.p. 98°).

Amine oxides have been shown to possess the structure $R_3N\rightarrow O$, in which the nitrogen atom is *tetra*-covalent.

QUESTIONS

1. How would you distinguish between primary, secondary and tertiary aliphatic amines ?

What are quaternary ammonium compounds ? Give one example. (*Calcutta, B.Sc., 1958*)

2. Outline methods available for the preparation of aliphatic primary amines. How may primary, secondary and tertiary aliphatic amines be distinguished from one another ? (*Andhra, B.Sc., 1954*)

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[1] *e.g.*, Benzyl chloride, $C_6H_5CH_2Cl$.

3. Give the general methods for the synthesis of primary amines. How would you distinguish between primary, secondary and tertiary amines? (*Travancore, B.Sc., 1954*)

4. How are primary, secondary and tertiary amines isolated in a state of purity from a mixture containing the three amines? By what tests are they distinguished from each other? (*Nagpur, B.Sc., 1950*)

5. (*a*) Describe chief methods of preparing monomethylamine. Give equations only.

(*b*) Describe Hinsberg method of separating primary, secondary and tertiary amines from a mixture containing all the three. (*Agra, B.Sc., 1954*)

6. Give in detail the methods of separation of primary, secondary and tertiary amines. How do you distinguish the three classes of amines from one another? (*Punjab, B.Sc., 1963*)

7. Describe briefly the methods you would employ to determine the mode of linkage of nitrogen atom in a substance having the molecular formula, C_3H_9N. (*Jammu & Kashmir, B.Sc., 1959*)

8. What are amines? How are they classified, and how may the different classes be distinguished and separated from one another? (*Aligarh, B.Sc., 1955*)

9. Give an account of the classification and isomerism of amines. By what methods can methylamine be prepared and what are its properties? (*Karnatak, B.Sc., 1955*)

10. How are aliphatic primary amines prepared? If you are given a mixture of primary, secondary and tertiary amines, how would you prepare pure specimens of each? Explain the chemistry underlying their separation. (*Rangoon, B.Sc., 1956*)

11. How would you distinguish between a primary, a secondary and a tertiary amine? What are metameric amines? Give examples. (*Gauhati, B.Sc., 1956*)

12. Describe methods for the preparation of Aliphatic amines. In what respects the aromatic amino compounds differ from them? Discuss the structure of quaternary ammonium compounds. (*Punjab, Pakistan, B.Sc., 1956*)

13. How are aliphatic primary amines prepared? Describe their important chemical reactions.

How is a mixture of primary, secondary and tertiary amines separated into respective constituents? (*Poona, B.Sc., 1957*)

14. Classify the nitrogenous aliphatic compounds. Describe the preparation of primary, secondary and tertiary amines free from one another. Mention the action of nitrous acid on each. (*Aligarh, B.Sc., 1957*)

15. Describe briefly Hofmann's method of preparing the aliphatic amines and state their properties. How would you distingush primary, secondary and tertiary amines? (*Gauhati, B.Sc, 1957*)

16. What are amines? How would you separate aliphatic amines (primary, secondary, tertiary and quaternary) occurring together in a mixture? Compare and contrast the properties of aliphatic and aromatic primary amines. (*Rajasthan, B.Sc., 1962*)

17. Describe the action of acetic anhydride, nitrous acid and benzenesulphonyl chloride on primary, secondary and tertiary amines.

How will you obtain (1) ethylamine from an amide, (2) *n*-butylamine from a nitrite, (3) *n*-propylamine from an aldehyde. (*Lucknow, B.Sc., 1962*)

18. How is methylamine prepared from (*a*) methyl alcohol; (*b*) formaldehyde; and (*c*) acetamide? Write equations.

Describe the physical and chemical properties of methylamine. What are quaternary ammonium compounds? Give examples. (*Calcutta, B.Sc., 1961*)

19. What are amines ? How are the aliphatic primary, secondary and tertiary amines separated from mixtures ? Give equations.

How would you identify a primary amine ? (*Gauhati, B.Sc., 1962*)

20. How would you distinguish between a primary, a secondary and a tertiary amine ? What are metameric amines ? Give examples. (*Utkal, B.Sc., 1962*)

21. (*a*) How will you obtain (*i*) Eihylamine from an amide, (*ii*) *n*-butyl amine from an oxime, (*iii*) N-acetyl N-propylamine from ethyl cyanide ?

(*b*) Describe the action of acetic anhydride, nitrous acid and benzene sulphonyl chloride on primary, secondary and tertiary amines. (*Lucknow, B.Sc., 1962*)

22. Give the structural formulae and names of the eight isomeric amines of the general formulae $C_4H_{11}N$. How will you identify them ?

(*Lucknow, B.Sc., 1959*)

23. State how primary amines may be prepared from : (*a*) Aldehydes, (*b*) Ketones. and (*c*) Acids.

Illustrate two methods by which primary, secondary and tertiary amines may be distinguished. (*Lucknow, B.Sc., 1962*)

24. Give the general methods of preparing aliphatic primary amines. How would you distinguish between primary, secondary and tertiary amines ?

(*Kerala, B.Sc., 1957*)

25. How are aliphatic amines prepared ? Give their general properties. How do you distinguish the various types of amines ? (*Bombay, B.Sc., 1958*)

26. Write an account of the properties, reactions, and methods of preparation of aliphatic amines. Classify the amines and indicate the differential behaviour of the various types. (*Jammu & Kashmir, B.Sc., 1950*)

27. What are amines ? Give formulae for two primary, two secondary and one tertiary aliphatic amine, name them. Describe the methods employed in separating these amines occurring together in a mixture. (*Rajasthan, B.Sc., 1960*)

28. Outline the methods available for the preparation of aliphate primary amines. How may primary, secondary and tertiary aliphatic amines be distinguished from one another. (*Venkateswara, B.Sc., 1960*)

29. How are primary, secondary and tertiary amines prepared ? How are they distinguished from one another ? (*Andhra, B.Sc., 1961*)

30. What are amines ? Give a method of preparing secondary amines unmixed with primary and tertiary. Describe a method by which these amines can be separated when in a mixture. (*Allahabad, B Sc., 1952*)

31. What do you understand by Ascent and Descent of Homologous Series ? How may the following conversions be effected :

(*a*) Ethyl alcohol into methyl alcohol ; (*b*) Methyl alcohol into ethyl alcohol ; (*c*) Acetic acid into propionic acid ; (*d*) Propionic acid into acetic acid ; (*e*) Acetamide into methylamine ?

32. Describe Hofmann's method of separation of primary, secondary and tertiary amines. What is the action of (*a*) nitrous acid, (*b*) Grignard's reagent on these amines ? What is the practical utility of these reactions ?

(*Rajputana, B.Sc , 1953*)

33. (*a*) Describe chief methods of preparing monomethylamine. Give equations only.

(*b*) Describe Hinsberg method of separating primary, secondary and tertiary amines from a mixture containing all the three. (*Agra, B Sc., 1950*)

34. A substance gave the following results on analysis : 0·2500 gm. gave 0·6027 gm. CO_2 and 0·339 gm. H_2O.

0·2000 gm. gave 53 4 ml. of N_2 at 20° and 750 mm.

Its vapour density was 37.

When heated with an excess of methyl iodide, it yielded a salt, 0·2149 gm. of which required 20·00 ml. N/20 $AgNO_3$ for complete precipitation. What was the substance ? [*Ans.* Ethyldimethylamine, $C_2H_5(CH_3)_2N$]

35. A compound, on analysis, shows 40·00% C, 13·33% H and 46·67% N. When vaporized, 0·268 gm. of the compound occupies 100 ml. calculated at N.T.P. A 0·2 gm. sample of the compound, treated with nitrous acid, evolves 149·3 ml. of nitrogen, calculated at N.T.P. Give graphical formula of the compound. (*Calcutta, B.Sc., 1956*)

Ans. $H_2N.CH_2.CH_2.NH_2$.

36. A compound, on analysis, shows C=40·0% H=13·33% and N=46·67%. When vaporized, 0·268 g. of this compound occupies 100 c.c. calculated at N.T.P. 0·2 gm. sample of the compound treated with nitrous acid gives 149·3 c.c. of N_2 calculated at N.T.P. Assign structure to the compound. (*Calcutta, B.Sc., 1956*)

Ans. Ethylenediamine, $NH_2.CH_2.CH_2.NH_2$ or Ethylidenediamine, $CH_3CH(NH_2)_2$.

37. An aliphatic monoamine has a vapour density of 36. On heating the amine with excess of methyl iodide for a long time, a quaternary salt containing 55 per cent of iodine is produced. What is the structural formula of the amine ? (I=127). (*Punjab, B.Sc., 1958*)

Ans. $(C_2H_5)_2NH$; $CH_3NHCH_2CH_2CH_3$; $CH_3NHCH(CH_3)_2$.

38. A compound X gave the following figures upon combustion : 0·236 gm. yielded 0·528 gm. carbon dioxide and 0·324 gm. water. In a nitrogen determination, according to Dumas, 0·295 gm. gave 56 c.c. of nitrogen, measured at N.T.P. X is a monoacid base ; its platinichloride contains 36·93 per cent Pt. What is its empirical and molecular formula ? Write down all the possible constitutional formulae for the compound and suggest how you would distinguish them from one another. (Pt=195) (*Agra, B.Sc., 1960 ; Delhi, B.Sc., 1958*)

Ans. Empirical formula, C_3H_9N ; molecular formula, C_3H_9N ; constitutional formulae : (*i*) $CH_3CH_2CH_2NH_2$, (*ii*) $(CH_3)_2CHNH_2$, (*iii*) $CH_3NHCH_2CH_3$, (*iv*) $(CH_3)_3N$.

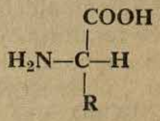
CHAPTER THIRTY-ONE

AMINO ACIDS

1. General.—Amino acids are derived from the carboxylic acids by the replacement of the hydrogen of the hydrocarbon radical by the amino-group, —NH_2. As in the case of the hydroxy acids, they are designated as α-, β-, γ-, etc., substituted acids, according to the position of the NH_2 group with respect to the carboxyl group.

α-Amino acids are of great physiological importance, as they are the structural units of which all the protein molecules are built up. When proteins are submitted to hydrolysis, they all give α-amino acids. So far, 22 α-amino acids have been thus obtained from proteins. Of these, 10 are "*essential*" amino acids, they *must* be present in the proteins of our food. Others are synthesized in the body when required.

α-Amino acids with the exception of glycine, have asymmetric carbon atoms, and are, therefore, capable of exhibiting **stereoisomerism.** It is important to note that all amino acids obtained from proteins have the **L-configuration**, shown in the margin. Amino acids having the D-configuration have no food value whatever. They have been prepared synthetically, and some are of importance as being component parts of antibiotic molecules.



$$\begin{array}{c} \text{COOH} \\ | \\ \text{H}_2\text{N—C—H} \\ | \\ \text{R} \end{array}$$

2. Preparation of Amino Acids by Hydrolysis of Proteins.—Hydrolysis of proteins, by boiling with dilute mineral acids, yields *mixtures* of amino acids from which the components may be separated only with difficulty. If a protein is rich in a particular amino acid, that acid can be separated more or less easily from the others by fractional crystallization. Thus, glycine (aminoacetic acid) may be prepared from glue, and glutamic acid from wheat gluten.

Fischer's method of separation of individual amino acids from the products of hydrolysis of proteins consists in the esterification of the mixture, separating the esters by fractional distillation, and hydrolyzing each of the esters separately to recover the amino acid.

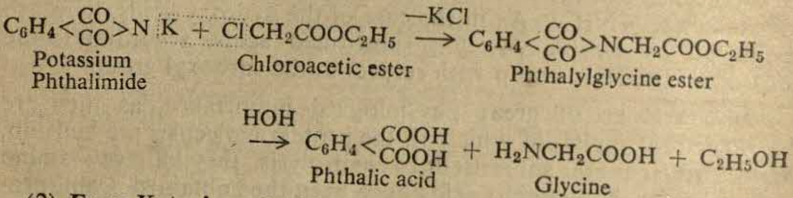
3. Synthesis of Amino Acids.—Synthesis of amino acids is carried out either for the preparation of acids not obtainable from natural sources or for establishing the structures of those that occur in nature. The following are the more important methods of synthesis :—

(1) **From halogen-substituted acids.**—

(*a*) When an α-halogen-substituted acid is treated with ammonia, the halogen atom gets replaced by an $-NH_2$ group :—

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + NH_3 \longrightarrow \underset{\text{Aminoacetic acid}}{CH_2(NH_2)COOH} + HCl$$

(*b*) In the above reaction, the primary monoamino acid first formed may react further with the halogen-substituted acid to give secondary and tertiary amino-acids. To avoid such side reactions, potassium phthalimide is used instead of ammonia (**Gabriel's phthalimide synthesis**), and the product is submitted to hydrolysis to recover the amino-acid :



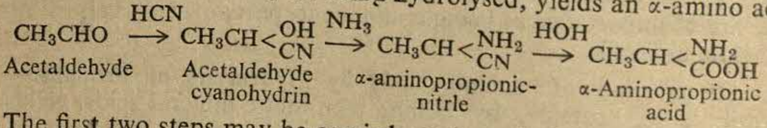
$$\underset{\text{Potassium Phthalimide}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\,K} + \underset{\text{Chloroacetic ester}}{Cl\,CH_2COOC_2H_5} \xrightarrow{-KCl} \underset{\text{Phthalylglycine ester}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NCH_2COOC_2H_5}$$

$$\xrightarrow{HOH} \underset{\text{Phthalic acid}}{C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix}} + \underset{\text{Glycine}}{H_2NCH_2COOH} + C_2H_5OH$$

(2) **From Ketonic and Aldehydic acids.** The acid is first converted into an oxime by treatment with hydroxylamine. The oxime is then reduced, by means of aluminium amalgam, to an amino acid :

$$\underset{\text{Pyruvic acid}}{CH_3COCOOH} \xrightarrow{NH_2OH} \underset{\text{Oxime of pyruvic acid}}{CH_3C(=NOH)COOH} \xrightarrow{H} \underset{\alpha\text{-Aminopropionic acid}}{CH_3CH(NH_2)COOH}$$

(3) **From Aldehydes and Ketones** (**Strecker's Aminonitrile Synthesis**). When an aldehyde or a ketone is treated with hydrogen cyanide, and the resulting cyanohydrin is allowed to react with ammonia, we get an amino nitrile. This, on being hydrolysed, yields an α-amino acid :



$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{HCN} \underset{\text{Acetaldehyde cyanohydrin}}{CH_3CH{<}\begin{matrix}OH\\CN\end{matrix}} \xrightarrow{NH_3} \underset{\alpha\text{-aminopropionic-nitrle}}{CH_3CH{<}\begin{matrix}NH_2\\CN\end{matrix}} \xrightarrow{HOH} \underset{\alpha\text{-Aminopropionic acid}}{CH_3CH{<}\begin{matrix}NH_2\\COOH\end{matrix}}$$

The first two steps may be carried out in a single operation by treating the aldehyde or ketone with ammonium cyanide (a mixture of an ammonium salt and a cyanide).

4. Physical Properties and Zwitterion Structure of Amino Acids.—The physical properties of amino acids resemble electrovalent compounds rather than typical covalent compounds.

They are crystalline solids melting at high temperatures (about 300°) with decomposition, and possessing comparatively high densities (*e.g.*, 1·6 for glycine). They are soluble in water and practically insoluble in absolute alcohol, ether and other organic solvents.

These and some other facts (see sec. 5) lead to the conclusion that the structure of amino acids is fundamentally different from that of typical organic compounds. We must regard their molecules as **dipolar ions** or **zwitterions**,[1] as they are more commonly termed, and not as possessing an ordinary covalent structure.

---

[1] German, *zwitter*, hermaphrodite, hybrid.

All evidence points to the conclusion that in the crystalline state, an amino acid exists *entirely* as the zwitterion. In aqueous solution, however, there is also a minute (almost negligible) proportion of covalent molecules.

$$H_3\overset{+}{N}CHRCO\overset{-}{O} \rightleftharpoons H_2NCHRCOOH$$

Zwitterion form (almost 100%) — Covalent form (negligible)

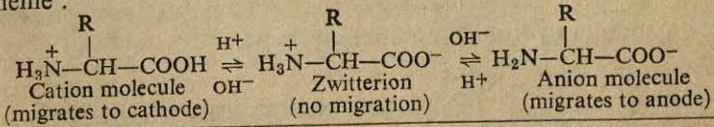
The addition of a reagent capable of reacting with the NH_2 group or the COOH group, makes the equilibrium shift to the right, until the whole of the Zwitterion has been exhausted.

5. Further Evidence for Zwitterion Structure.—

(1) **Dipole Moments.** The zwitterion structure of amino acids assumes the existence of centres of opposite charges within the molecule. The distance in centimeters between these centres multiplied by the magnitude of the charge is termed the **dipole moment** of the molecule. The dipole moments are generally expressed in terms of the Debye unit, D, which is equal to 1×10^{-18} esu.

The dipole moments of amino acids are exceptionally high. Thus, the value for glycine is about 15 D as compared with 2 to 3 D ordinarily met with among organic compounds. The β-, γ- and δ- etc. amino acids have progressively higher values, showing that the distances between the centres of the charges here are correspondingly greater. These facts are fully in accord with the the zwitterion structure of amino acids.

(2) **Isoelectric Point.** Another very interesting fact about amino acids that fully supports the zwitterion structure is that the direction in which amino acids migrate in an electric field depends on the *p*H value of the solution. When the solution is highly acidic (*e.g.* one with *p*H 1, prepared by dissolving the amino acid in HCl), the amino acid migrates towards the cathode, showing that it carries a positive charge. In alkaline solution (*e.g.* one with *p*H 9) it travels towards the anode showing that the charge on the molecule is negative. At an intermediate hydrion concentration, termed the **isoelectric point**, the amino acid *does not migrate at all*, showing that the *net* charge on the molecule is zero. At this point the amino acid is supposed to exits *entirely* (*i.e.* very nearly so) as the **zwitterion.** Addition of acid to such a solution results in the production of a **cation molecule** and of an alkali an **anion molecule**, as shown in the following scheme :



$$H_3\overset{+}{N}-\overset{R}{\overset{|}{C}}H-COOH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} H_3\overset{+}{N}-\overset{R}{\overset{|}{C}}H-COO^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_2N-\overset{R}{\overset{|}{C}}H-COO^-$$

Cation molecule (migrates to cathode) — Zwitterion (no migration) — Anion molecule (migrates to anode)

---

[1] X-ray measurements on glycine crystals give a distance of 2.96 angstrom units between the centre of the plus charge on the nitrogen atom and that of the minus charge assumed to be midway between the two oxygen atoms of the carboxylate group, $-COO^-$.

In the following table are given the isoelectric points of a few amino acids. It may be noted that for acids having one NH_2 group and one COOH group in the molecule, the value is in the neighbourhood of *p*H 6. When there are two NH_2 groups and only one COOH group, the isoelectric point is on the alkaline side (*e.g.*, *p*H 9·7 for lysine). On the other hand, the presence of two COOH groups and one NH_2 group, takes the isoelectric point to the acidic side (*e.g.*, *p*H 3·1 for glutamic acid).

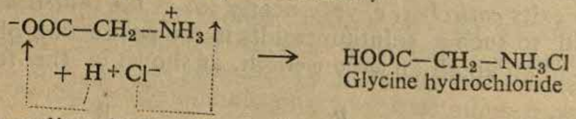
Amino acid	Isoelectric *p*H
Glycine, Aminoacetic acid, $CH_2(NH_2)COOH$	6·06
Alanine, α-Aminopropionic acid, $CH_3CH(NH_2)COOH$	6·11
Lysine, αε-diaminocaproic acid, $H_2N(CH_2)_4CH(NH_2)\ COOH$	9·70
Aspartic acid, amino-succinic acid $HOOCCH_2CH(NH_2)COOH$	2·98
Glutamic acid, α-aminoglutaric acid, $HOOC(CH_2)_2CH(NH_2)\ COOH$	3·08

At the isoelectric point, an amino acid[1] has the minimum solubility and can be obtained in the free state by crystallization. If concentration of the solution be carried out at any other *p*H value, only a salt containing, for example, Na^+ (or Cl^-) is obtained. A knowledge of the isoelectric points, therefore, is very important in the isolation of amino acids (and other amphoteric substances) from natural sources and synthetic reaction products.

(3) **Raman Spectra.**—A most conclusive proof of the zwitterion structure of amino acids is afforded by Raman spectra measurements. The Raman line characteristic of carboxylic acids in aqueous solution is of 1720 $cm.^{-1}$. This is *not* exhibited by amino-acids until converted into their hydrochlorides. Similarly, the Raman lines characteristic of unionized primary amines (which are 3300 and 3400 $cm.^{-1}$) are shown by amino acids only in alkaline solutions.

6. Reactions of Amino Acids.—As amino acids are amphoteric in nature, their chemical behaviour in acid and alkaline solutions is different. In a strongly acidic medium, they give the various reactions of the —COOH group, while in the presence of strong alkalis the typical reactions of the NH_2 group are exhibited.

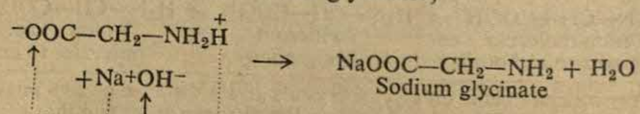
(1) **Salt Formation.** Amino acids react both with acids and with bases, giving salts. Thus, glycine (aminoacetic acid) with hydrochloric acid gives glycine hydrochloride,



$$^{-}OOC-CH_2-\overset{+}{N}H_3 + H^{+}Cl^{-} \longrightarrow HOOC-CH_2-NH_3Cl$$

Glycine hydrochloride

and with sodium hydroxide, sodium glycinate,



$$^{-}OOC-CH_2-NH_2\overset{+}{H} + Na^{+}OH^{-} \longrightarrow NaOOC-CH_2-NH_2 + H_2O$$

Sodium glycinate

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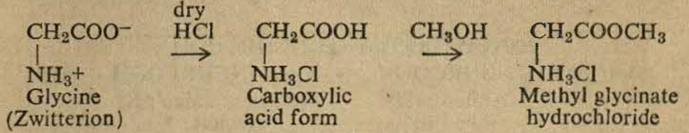
[1] The remarks apply equally well to proteins and other amphoteric substances.

(2) **Esterification.** The esterification of amino acids is effected in a strongly acidic medium. The hydrion of the acid (of which a large excess is used) makes the zwitterion pass into the COOH form which then reacts with the alcohol present to form the ester:—



$$\underset{\substack{\text{Glycine}\\\text{(Zwitterion)}}}{\begin{array}{l}CH_2COO^-\\ |\\ NH_3^+\end{array}} \xrightarrow{\substack{\text{dry}\\ HCl}} \underset{\substack{\text{Carboxylic}\\\text{acid form}}}{\begin{array}{l}CH_2COOH\\ |\\ NH_3Cl\end{array}} \xrightarrow{CH_3OH} \underset{\substack{\text{Methyl glycinate}\\\text{hydrochloride}}}{\begin{array}{l}CH_2COOCH_3\\ |\\ NH_3Cl\end{array}}$$

The reaction product is carefully neutralized with a calculated amount of *cold,* dilute alkali, to set free the ester.

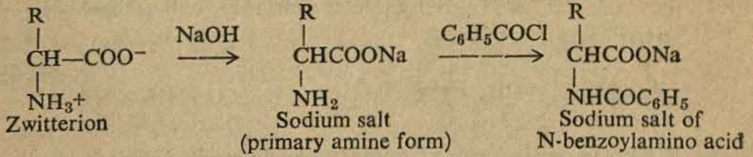
The **esters of amino acids** are *not* zwitterions, and therefore behave as normal covalent compounds possessing reactions both of primary amines and esters. They are generally water-insoluble liquids that can be distilled without decomposition under reduced pressure. Their formation, as already mentioned, is utilized in the separation of amino acids from their mixtures. They may also be employed for the preparation of amino acid amides (*e.g.* $NH_2CH_2CONH_2$) and amino alcohols (*e.g.*, $NH_2CH_2CH_2OH$).

(3) **Reaction with nitrous acid.** The NH_2 group in an amino acid reacts with nitrous acid ($NaNO_2$+excess acetic acid) in the normal manner with evolution of nitrogen,

$$\underset{\text{Glycine}}{\left\{\begin{array}{l}H_3\overset{+}{N}CH_2COO^- \rightleftharpoons\\ H_2NCH_2COO\end{array}\right\}} + HONO \rightarrow \underset{\text{Glycollic acid}}{CH_2(OH)COOH} + N_2 + H_2O$$

The reaction may be used for the preparation of hydroxy-acids and for the **estimation of NH_2 group** in amino acids.

(4) **Acetylation.** Amino acids may be acetylated or benzoylated in the presence of alkali (which serves to transform the zwitterion into the amino form and also to neutralize the HCl produced in the reaction). Thus, with benzoyl chloride we have:—



$$\underset{\text{Zwitterion}}{\begin{array}{l}R\\ |\\ CH{-}COO^-\\ |\\ NH_3^+\end{array}} \xrightarrow{NaOH} \underset{\substack{\text{Sodium salt}\\\text{(primary amine form)}}}{\begin{array}{l}R\\ |\\ CHCOONa\\ |\\ NH_2\end{array}} \xrightarrow{C_6H_5COCl} \underset{\substack{\text{Sodium salt of}\\\text{N-benzoylamino acid}}}{\begin{array}{l}R\\ |\\ CHCOONa\\ |\\ NHCOC_6H_5\end{array}}$$

The **N-benzoylamino-acids**, obtained by treating the reaction product (sodium salts) with dilute HCl, are sufficiently strong acids to combine with optically active bases (*e.g.* alkaloids) and are thus used for **resolving racemic amino acids** into their optically active components.

(5) **Formal titration.** Amino acids, because of their weakly acidic character, cannot be titrated in the usual way. It is, therefore, necessary first to block off the basic function of the amino group. In the formal titration method, due to Sorensen, an excess of formaldehyde is added to the amino-acid solution. This reacts with the

NH_2 group in a way which destroys its basic character. The carboxyl group, which is thus left free, can then be titrated with standard alkali with phenolphthalein as the indicator.

The reaction with formaldehyde is usually represented as under:

$$H_3\overset{+}{N}CHRCOO^- \rightleftharpoons H_2NCHRCOOH$$

$$CH_2O + H_2NCHRCOOH \rightarrow CH_2{=}NCHRCOOH + H_2O$$

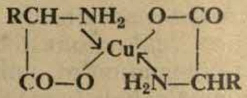
Amino-acid (neutral) — Methyleneamino acid (acidic)

$$2CH_2(NH_2)COOH + Ba(OH)_2 \rightarrow 2CH_3NH_2 + BaCO_3 + H_2O$$

Actually, however, it is more complex.

(6) **Carbylamine reaction.** Amino acids, like primary amines, give the carbylamine reaction.

(7) **Cupric sulphate reaction.** When cupric sulphate is added to an aqueous solution of an amino acid, a deep blue coloration results on account of the formation of a co-ordination complex[1], shown in the margin.



(8) **Decarboxylation.** Heating an amino acid with barium hydroxide solution removes carbon dioxide with the formation of a primary amine :—

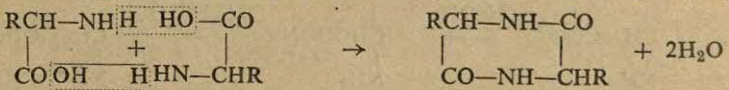
$$\underset{\text{Glycine}}{2CH_2(NH_2)COOH} + Ba(OH)_2 \rightarrow \underset{\text{Methylamine}}{2CH_3NH_2} + BaCO_3 + H_2O$$

(9) **Deamination.** Heating with hydriodic acid at 200° removes the amino group with the production of an unsubstituted carboxylic acid,

$$CH_2(NH_2)COOH + 3HI \longrightarrow CH_3COOH + NH_4I + I_2$$

7. Thermal Decomposition of Amino Acids.—Behaviour of amino acids on heating differs with the position of the —NH_2 group with respect to the —COOH group (compare hydroxy-carboxylic acids):—

(*i*) α-Amino acids lose two molecules of water between two molecules of the acid, giving cyclic diamides, called **diketopiperazines,**



$$\begin{array}{l} RCH{-}NH\,H \quad HO{-}CO \\ \quad | \qquad + \qquad | \\ CO\,OH \quad H\,HN{-}CHR \end{array} \rightarrow \begin{array}{l} RCH{-}NH{-}CO \\ \quad | \qquad\quad | \\ CO{-}NH{-}CHR \end{array} + 2H_2O$$

α-Amino-acid (2 mols.) — Diketopiperazine

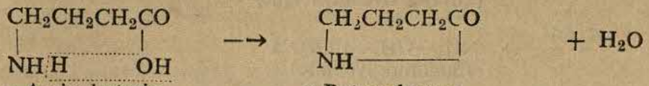
(*ii*) β-Amino acids lose ammonia when heated, yielding unsaturated acids; *e.g.*

$$\underset{\beta\text{-Aminopropionic acid}}{CH_2(NH_2)CH_2COOH} \longrightarrow \underset{\text{Acrylic acid}}{CH_2{=}CHCOOH} + NH_3$$

---

[1] The complex is a *non-electrolyte*. The central copper atom, as usual, is 4-covalent, the two amine groups being linked to it by co-ordinate links and the two carboxylic oxygens by covalent links. The amino-acid ion is, therefore, a *bidentate* chelating group. There are two 5-membered rings in the molecule and the complex, as a whole, is zero-electrovalent.

(*iii*) γ-and δ-amino acids readily lose water, yielding inner anhydrides, called **lactams** :



$$\underset{\text{NH H}\quad\text{OH}}{\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}} \longrightarrow \underset{\text{NH}}{\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}} + H_2O$$

γ-Aminobutyric, γ-Butyro-lactam

8. Aminoacetic Acid, H_2NCH_2COOH or $H_3NCH_2COO^-$, *Glycine*, Glycocoll.

Occurrence. This acid occurs as benzoylglycine, (C_6H_5CO)-$NHCH_2COOH$, or hippuric acid (*hippos*, horse) in the urine of the horse and other herbivorous animals. As trimethylglycine, it is present in beet-root molasses. Glycine is also one of the component units of certain proteins. Thus, gelatin contains 25 per cent and silk fibroin 44 per cent of this acid.

Preparation. Glycine is usually prepared by slowly adding an aqueous solution of chloroacetic acid to strong ammonia (sp. gr. 0·88) to which an equal volume of a saturated solution of ammonium carbonate[1] has previously been added,

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + 2NH_3 \rightarrow CH_2(NH_2)COOH + NH_4Cl.$$

The flask containing the reaction mixture is tightly corked, and allowed to stand for 24 to 48 hours at room temperature. The liquid is then transferred to a distillation flask, and distilled under reduced pressure (using a water filter pump), until the volume is reduced to about one-fourth. The residual concentrated solution containing glycine and ammonium chloride is cooled, and methyl alcohol is added to it to precipitate the amino acid.[2] The mixture is allowed to stand in an ice-box for 4 to 6 hours to permit crystallization. The crystals of glycine are filtered at the pump, washed well with methyl alcohol[3] and then with a little ether.

An alternative (though not so satisfactory) method of separating glycine from the reaction product consists in concentrating the solution, adding cupric carbonate and crystallizing out the cupric derivative. The latter is then dissolved in water and decomposed with H_2S to set free the amino acid. The cupric sulphide is filtered off, and the filtrate concentrated to crystallization.

Properties. Aminoacetic acid forms colourless crystals. When heated, it darkens at 237° and melts (with decomposition) at 240°. The acid is soluble in water, but insoluble in anhydrous alcohol, ether and benzene.

Reactions of glycine are the same as those of other amino acids (sec. 6), and are summarized below :—

$$\underset{\text{Zwitterion form}}{H_3\overset{+}{N}CH_2COO^-} \rightleftharpoons \underset{\text{Covalent form}}{H_2NCH_2COOH} \longrightarrow$$

(Aminoacetic Acid)

---

[1] The addition of ammonium carbonate serves to increase the yield.

[2] The ammonium chloride remains behind in solution.

[3] The product (which contains ammonium chloride as the chief impurity) may be purified by washing with methyl alcohol.

(1) $\xrightarrow{HCl} NH_3Cl-CH_2-COOH$
(Glycine hydrochloride)

(2) $\xrightarrow{NaOH} NH_2-CH_2-COONa$
(Sodium glycinate)

(3) $\xrightarrow{\text{Esterification}} NH_2CH_2COOC_2H_5$
Ethyl glycinate

(4) $\xrightarrow{HNO_2} CH_2(OH)COOH + N_2 + H_2O$
Glycollic acid

(5) $\xrightarrow{C_6H_5COCl} C_6H_5CONHCH_2COOH$
N-Benzoylglycine

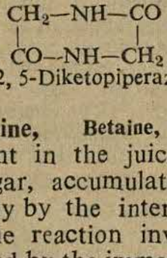
(6) $\xrightarrow{HCHO} CH_2{=}N-CH_2-COOH$
Methyleneaminoacetic acid

(7) $\xrightarrow{CuSO_4aq}$ copper glycine (formula in margin, p. 466)

(8) $\xrightarrow[\text{(decarboxylation)}]{Ba(OH)_2aq} CH_3NH_2$
Methylamine

(9) $\xrightarrow[\text{(deamination)}]{HI\ at\ 200^\circ} CH_3COOH$
Acetic acid

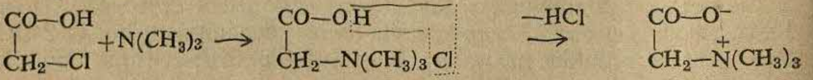
(10) $\xrightarrow{\text{Dehydration}}$



$$\begin{array}{l}CH_2-NH-CO\\|\qquad\qquad\ \ |\\CO-NH-CH_2\end{array}$$

2, 5-Diketopiperazine

9. **Trimethyl glycine,** **Betaine,** $(CH_3)_3\overset{+}{N}-CH_2-COO^-$.—This compound is present in the juice of sugar-beet, and, during the manufacture of sugar, accumulates in the molasses. It may be obtained synthetically by the interaction of chloroacetic acid and trimethylamine. The reaction involves the direct combination of the reactants followed by the immediate splitting off of a molecule of hydrogen chloride from the resulting quaternary ammonium compound.



$$\begin{array}{l}CO-OH\\|\\CH_2-Cl\end{array}+N(CH_3)_3\longrightarrow\begin{array}{l}CO-OH\\|\\CH_2-N(CH_3)_3Cl\end{array}\xrightarrow{-HCl}\begin{array}{l}CO-O^-\\|\\CH_2-\overset{+}{N}(CH_3)_3\end{array}$$

This synthesis of betaine shows that the three methyl groups are all linked to nitrogen. Hence the compound possesses the structure given above.

Betaine forms large colourless crystals, containing one molecule of water. When heated, it undergoes decomposition, yielding trimethylamine. This reaction forms the basis of the manufacture of trimethylamine from beet-molasses.

10. **Other Amino Acids** :—

Alanine, *α-aminopropionic acid,* $CH_3CH(NH_2)COOH$, and **serine** α-amino-β-hydroxy-propionic acid, $CH_2(OH)CH(NH_2)COOH$, are both obtained by the hydrolysis of silk and are optically active.

Leucine, *α-amino-isobutyl-acetic acid,* $(CH_3)_2CHCH_2CH(NH_2)COOH$ and **isoleucine,** *α-amino-β-methyl-valeric acid* $CH_3CH_2CH(CH_3)CH(NH_2)COOH$, are found in nature associated with each other. They are formed in considerable quantities during the putrefaction of proteins, or when the latter are hydrolysed with acids or alkalis.

Ornithine, *α,δ-diamino-valeric acid,* $CH_2(NH_2)CH_2CH_2CH(NH_2)COOH$ and **lysine,** α,ε-diaminocaproic *acid* $NH_2(CH_2)_4CH(NH_2)COOH$, are both diamino-monocarboxylic acids. They, therefore, possess basic properties.

Aspartic acid, *amino-succinic acid,* $COOHCH(NH_2)CH_2COOH$, and **glutamic-acid,** *α-amino glutaric acid,* $COOHCH(NH_2)CH_2COOH$, being monoamino dicarboxylic acids, possess an acid reaction. Both of them are formed as products of hydrolysis of various animal and vegetable proteins.

Glutamic acid is manufactured from wheat gluten (which contains about 30 per cent of glutamic acid). Its **monosodium salt** is used as a flavouring ingredient for soups and sauces, etc., and as a table condiment. It imparts to food at pleasant meat-like flavour.

QUESTIONS

1. What are amino acids? How are they related to proteins? Give the preparation and properties of glycine. *(Rajasthan, B.Sc., 1962)*

2. Write an essay on Amino acids. *(Lucknow, B.Sc., 1962)*

3. Write a short note on Amino acids. *(Lucknow, B.Sc., 1961)*

4. Give the synthesis of Alanine. *(Lucknow, B.Sc., 1961)*

5. Describe two methods of preparing amino acids. What specific reactions are employed for detecting proteins? *(Agra, B.Sc., 1958)*

6. What are amino acids? How are they prepared? Mention their important properties. What is their physiological importance? What light do they throw on the structure of proteins? *(Gorakhpur, B.Sc., 1959)*

7. Write a note on Aminoacetic acid. *(Punjab, B.Sc., 1963)*

8. Describe some important methods used for preparing amino acids. Mention their important properties and show their chemical relationship with proteins. *(Agra, B.Sc., 1956)*

9. Give an account of the methods that have been developed for the synthesis of α-amino acids. *(Travancore, B.Sc., 1956)*

10. What methods would you suggest for the preparation of Glycine NH_2CH_2COOH? What properties would such a compound possess? Give its important reactions. *(Nagpur, B.Sc., 1957)*

11. Give an account of the preparation of amino acids from natural sources and by synthetic methods. Discuss the structure of glycine. What is the effect of heat on it, and on other amino acids? *(Travancore, B.Sc., 1957)*

12. A crystalline organic substance, *A*, was found to possess the empirical formula $C_3H_7O_2N$. 0.26 gm. of the substance when treated with an excess of nitrous acid gave 67.2 ml. of nitrogen measured at N.T.P. The reaction product, when evaporated to dryness and heated strongly with soda-lime, left a residue, which when treated with hydrochloric acid evolved carbon dioxide. The substance, *A*, when heated evolved ammonia; the residual liquid, *B*, was found to decolorize bromine and also dilute alkaline potassium permanganate. Assign structural formulae to both *A* and *B*.
[*Ans. A* : β-Amino-propionic acid, $CH_2(NH_2)CH_2.COOH$.
B : Acrylic acid $CH_2=CHCOOH$.]

13. Give the structural formula of betaine. How is this substance prepared? How may it be converted into trimethylamine?

West Bengal

CHAPTER THIRTY-TWO

PROTEINS

1. Physiological Importance.—Proteins are naturally-occurring colloidal substances, which are **largely composed of amino-acid residues usually linked together by an amide type of linking.** Like fats and carbohydrates, proteins are of great physiological importance, and are indispensable components of animal and vegetable organisms. They form the most important part of human and animal food, as is apparent from the fact, that, while an animal can exist for a very long period without fats and carbohydrates, its death is certain if proteins be withdrawn from its food. Indeed, at one time it was considered that proteins alone were sufficient to maintain life, and that the most efficient and economical diet was one containing a maximum proportion of proteins. Recent research on nutrition, however, has shown this view to be incorrect. Further, it has been found that the digestibility of various proteins differs very widely. The investigation of the chemical nature of various proteins and other food materials and their respective digestibility today form the most important part of the study of animal nutrition.

2. Composition.—Proteins differ from the other two classes of foodstuffs, namely fats and carbohydrates, in composition. While the latter are made up of carbon, hydrogen and oxygen, proteins, in addition to these three elements, contain nitrogen, and, in some cases, also sulphur and phosphorus. The percentage of the six elements present in proteins varies for different types within the limits given below:—

C......50.5 to 54·5 per cent. N......15·0 to 17·5 per cent.
H.......6.5 „ 7·5 „ S.......0·6 „ 2·2 „
O......21·5 „ 23·5 „ P......0·42 „ 0·84 „

3. Physico-chemical Properties.—*Colloidal Nature.* Proteins are colloidal substances, and are unable to pass through animal and vegetable membranes. This fact is utilized in preparing them in a more or less pure condition.

(2) *Reversible Precipitation by Neutral Salts.* When sodium chloride, ammonium sulphate, or some other alkaline-earth salt, is added to a protein solution, the osmotic pressure of the latter gradually falls, until at definite concentration of the salt the protein is thrown out of solution. The protein thus precipitated is found to possess its original characters, and after being filtered, may be redissolved in water. This fact is utilized for the separation of certain proteins.

The salts most commonly employed for the separation of proteins are ammonium sulphate, magnesium sulphate, zinc sulphate and sodium chloride.

(3) *Coagulation*. When proteins are subjected to the action of heat, or certain reagents, such as alcohol, acetone, solutions of heavy-metal or alkaline-earth salts, they are coagulated. The product, unlike that in (2), cannot be reconverted into the original substance. During coagulation, the protein, as we say, is *denatured*. Coagulation of proteins by suitable reagents is employed for removing them from a solution and for their quantitative estimation.

(4) *Amphoteric Character*. Proteins, like amino acids, contain the basic (amino) as well as the acidic (carboxyl) group, and are, therefore, **amphoteric electrolytes with a zwitterion structure.**

(5) *Crystallization*. Though colloidal in nature, proteins can take up the crystalline form. Protein crystals occur in nature as the aleurone grains found abundantly in the seeds of plants. On the other hand, a number of proteins that do not occur in nature in the crystalline state have been obtained in this form in the laboratory. Thus, Hofmeister, in 1889, obtained egg albumin[1] in the crystalline state. Albumin from the horse serum, haemoglobin, and globulins from plant seeds have been obtained in the crystalline form.

(6) *Optical Activity*. Solutions of proteins are optically active, being in almost all cases levorotatory (compare amino acids).

4. **Reactions of Proteins.**—Though proteins are divided into several classes, they give a series of very characteristic reactions which are employed for their identification. No single reaction can in itself serve as a reliable test for the presence or absence of proteins, since all proteins do not give all reactions. It is, therefore, necessary to perform a number of reactions before a conclusion is drawn.

For a study of the general reactions of proteins given below, a solution of egg-white is prepared as follows: Egg white[2] is beaten, filtered through calico and diluted to 20 times its original bulk. A precipitate of *ovomucin* separates, but it passes into solution on adding a little salt solution (sodium chloride or ammonium sulphate).

The reactions are divided into three classes.

(*A*) **Colour Reactions.** The colour reactions indicate the various constituent units of the protein molecule.

(1) *Biuret Reaction*. This is characteristic of a repetition of the group—CONH—.

Expt. 1. To some of the protein solution add sodium hydroxide, and then a dilute solution of cupric sulphate (1 per cent), a drop at a time, mixing after each addition; a violet coloration appears.

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[1] The method consists in mixing a solution of egg white with an equal bulk of concentrated ammonium sulphate, filtering off the precipitated globulins, and then acidifying the filtrate with acetic acid.

[2] This has a faintly alkaline reaction and contains about 10 to 12 per cent of protein.

(2) *Xanthoproteic Reaction.* This reaction is due to the formation of nitro-compounds with the aromatic units present in a protein. The yellow stain produced on the skin by nitric acid is a familiar example of this reaction.

Expt. 2. Heat some of the protein solution with concentrated nitric acid ; a yellow colour results, which changes to orange on the addition of ammonia.

(3) *Millon's Reaction.* The reaction is due to the presence of a phenolic unit in the protein molecule. The reagent consists of an aqueous solution of mercuric nitrate containing free nitrous acid.

Expt. 3. Add Millon's reagent[1] to some of the protein solution ; a white precipitate is formed, which turns red on heating.

(4) *Adamkiewicz' Reaction.* This reaction is due to the indole group in a protein molecule.

Expt. 4. Add excess of glacial acetic acid (or better a small quantity of a solution of glyoxalic acid in glacial acetic acid) to the protein solution, and then pour some concentrated sulphuric acid down the side of the tube, so that it forms a separate layer at the bottom. A reddish-violet coloration appears at the junction of the two layers which gradually spreads throughout the solution.

(5) *Molisch's Reaction.* This reaction is due to the presence of the carbohydrate unit in a protein molecule.

Expt 5. Mix a few drops of α-naphthol solution[2] with the protein solution, and run concentrated sulphuric acid under the solution ; a purple red ring is formed at the junction of the two layers.

(6) *Lead Sulphide Test.* This test is due to the presence of sulphur. The hydrogen sulphide set free reacts with the lead salt to give lead sulphide.

Expt. 6. Add a drop of lead acetate solution to some of the protein solution ; and then sufficient caustic soda to redissolve the ppt. first formed. Boil the liquid ; a brown to black coloration is developed.

(*B*) **Coagulation Reactions :** (1) *Action of Heat.* Coagulation of a protein in aqueous solution occurs if the solution be rendered faintly acid, and then heated ; so long as the reaction is alkaline, coagulation does *not* occur.

Expt. 7. In two separate test-tubes place equal quantities of protein solution, and to one of these add a few drops of dilute acetic acid. Heat the two tubes ; an opalescene is produced in the first tube, while in the other a cloudiness occurs, and then a flocculent precipitate of coagulated protein is formed. The precipitate is insoluble in dilute acids and alkalis in the cold, but on heating with sodium hydroxide, it gradually passes into solution.

(2) *Action of Alcohol.* If an excess of alcohol be added to an aqueous solution of a protein, the latter is precipitated. The precipitate, when fresh, is capable of re-dissolution in water, but on prolonged contact with alcohol it loses this property, the protein being coagulated.

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[1] Millon's reagent is prepared by dissolving 5 ml. of mercury in 100 ml. of concentrated nitric acid, and diluting with 2 volumes of water.

[2] Molisch's reagent is made by dissolving 14.4 gm. of α-napthol in alcohol and making up the volume to 100 ml. with alcohol.

(3) *Heller's Test.*

Expt 8. Take some protein solution in a test-tube, and pour concentrated nitric acid down the side of the tube, so that the acid forms a separate layer at the bottom. A white ring of coagulated protein is formed at the junction of the two layers.

(*C*) **Precipitation Reactions.** These may be further divided into two groups :

(I) PRECIPITATION BY HEAVY-METAL SALTS

(1) *Mercuric Chloride.*

Expt. 9. Add 3 or 4 drops of mercuric chloride to some of the protein solution ; a heavy, white precipitate of the mercury compound is formed.

Add now some saturated sodium chloride solution ; the precipitate is redissolved.

Add a few drops of hydrochloric acid to the above solution ; the mercury compound is again precipitated.

(2) *Copper Sulphate.*

Expt. 10. Add 3 or 4 drops of copper sulphate solution ; a bluish violet precipitate is formed.

Now, add sodium hydroxide solution ; the precipitate dissolves, yielding a violet solution (*biuret reaction*).

(3) *Ferric chloride* yields a precipitate soluble in excess of the reagent.

(4) *Lead acetate* and *basic lead acetate* yield white precipitates.

(II) PRECIPITATION BY ALKALOID REAGENTS

Certain reagents give precipitates with most alkaloids, and are consequently called **alkaloid reagents.** Proteins, like alkaloids, are weakly basic substances, and give precipitates with the so-called alkaloid reagents.

(1) *Hydroferrocyanic Acid.* This test is often employed for detecting albumin in the urine.

Expt. 11. Take some protein solution in a test-tube. Add a few drops of glacial acetic acid and then, drop by drop, potassium ferrocyanide solution. A voluminous precipitate is formed.

(2) *Picric Acid* produces a yellowish precipitate.

(3) *Tannic Acid* produces a brownish precipitate.

(4) *Phosphotungstic Acid,* when added to a protein solution, previously acidified with hydrochloric acid, produces a white precipitate. Since the reagent brings about complete precipitation of proteins, it is frequently employed for their removal from solution.

5. **Constitution of Proteins.**—As already mentioned, proteins are hydrolysed by acids, yielding a mixture of amino acids. This led chemists to believe that the molecules of simple proteins consist of combination of amino acid molecules linked together through amino and carboxyl groups. This hypothesis was confirmed by the

researches of Emil Fischer, who succeeded in linking together amino acid molecules, step by step, and named the compounds, thus synthesized **polypeptides.** To take the simplest case, two molecules of glycine may be linked together by bringing together the acid and its chloride.

$$\underset{\text{Glycyl chloride}}{CH_2(NH_2)CO\,Cl} + \underset{\text{Glycine}}{H\,NHCH_2COOH} \longrightarrow$$

$$\underset{\text{Glycyl glycine}}{CH_2(NH_2)CO{-}NHCH_2COOH} + HCl$$

The resulting compound, glycyl-glycine, is a **dipeptide.** When a dipeptide is treated with phosphorus pentachloride in acetyl chloride solution, its COOH group is changed to COCl. The resulting acid chloride, when treated with a third molecule of an amino acid yields a **tripeptide**, such as—

$$\underset{\text{Diglycylglycine}}{CH_2(NH_2)CO{-}NHCH_2CO{-}NHCH_2COOH}$$

Proceeding in this manner, Fischer succeeded in preparing an **octadecapeptide**, in which 18 amino-acid molecules have been linked together. It consists of 15 glycine and 3 leucine units, and closely resembles natural proteins. It is a colloidal substance, is hydrolysed by the enzyme **trypsin** (present in the pancreatic juice) into the amino acids, and gives the colour reactions characteristic of proteins.

A further evidence of the **polypeptide nature of proteins** is that polypeptides have actually been isolated from the products of hydrolysis of proteins.

QUESTIONS

1. What are *proteins* ? Why are they regarded as one of the most important groups of organic compounds ? Give their general physico-chemical characters and characteristic reactions.

2. What are proteins and polypeptides ? What is the relationship between them ? How have the polypeptides been synthesised ? (*Bombay, B.Sc., 1952*)

3. What specific reactions are employed for detecting proteins ? (*Agra, B.Sc., 1958*)

4. Discuss the results obtained by hydrolysis of the proteins. (*London, B.Sc., 1932*)

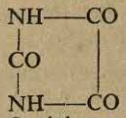
5. Give the principal methods of synthesizing amino acids. Show how amino acids can be converted into polypeptides. (*Bombay, B.Sc., 1956*)

6. What are proteins ? How are they classified ? Discuss their important reactions. What is their importance ? Discuss their relationship with amino acids. (*Agra, B Sc , 1958.*)

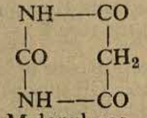
CHAPTER THIRTY-THREE

UREIDES AND PURINES

1. Cyclic Ureides.—We have seen that urea reacts with acid chlorides and esters in the same way as ammonia, yielding *ureides*. The simple ureides of monocarboxylic acids (such as acetylurea, $CH_3CONHCONH_2$) are of little importance. The **cyclic ureides** of certain dicarboxylic acids, notably those of oxalic and malonic acids, are of considerable interest, as from them can be derived all the members of the uric acid group.

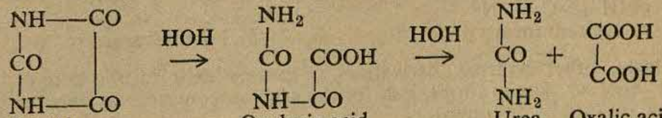


Oxalylurea
(Parabanic acid)



Malonylurea
(Barbituric acid)

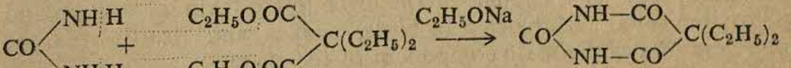
Most of the cyclic ureides form beautiful crystals. Like amides, they are decomposed by alkalis. On prolonged heating with dilute alkalis, they are hydrolysed to give first **ureido-acids** and then urea and the dicarboxylic acid :—



Oxalylurea Oxaluric acid Urea Oxalic acid

2. Barbituric Acid, *Malonyl Urea.*—This compound is of special interest both from the theoretical and the practical points of view. Its formation by the condensation of urea with malonic ester in presence of sodium ethoxide (page 384, reaction 2) constitutes the first step in Fischer's synthesis of uric acid (page 480). Some of its C-alkyl and C-aryl derivatives are used as hypnotics.

3. Veronal. *C-Diethylmalonylurea, C-Diethylbarbituric Acid.*—This important compound is prepared on a commercial scale by the condensation of diethylmalonic ester with urea in the presence of sodium ethoxide,

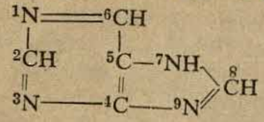
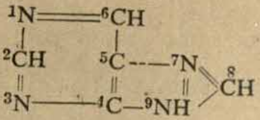


Urea Diethylmalonic ester Veronal

$+2C_2H_5OH$

Veronal and certain other C-alkyl and C-aryl derivatives of barbituric acid are used in medicine as hypnotics.

4. Purines.—Uric acid and some other structurally related compounds are cyclic diureides, as they contain two urea residues in the molecule. They are all derived from the same parent compound, named, by Fischer, **purine** (L. *purum uricum*), which is a tautomeric substance with formulae I and II given below :

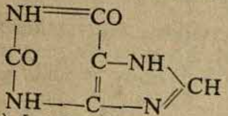
(I)

(II)


From these formulae we see that the purine molecule consists of two rings, one 6-membered, and the other 5-membered, fused together at positions 5 and 6 The nitrogen and the carbon atoms forming the two rings are numbered as given above for the sake of reference.

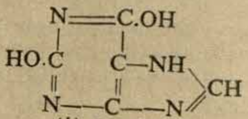
Purine itself does not occur in nature, but was synthesized by Fischer. It is a readily soluble, crystalline compound melting at 212°.

5. Purine Derivatives.—The purine derivatives possess tautomeric formulae[1] corresponding to formulae I and II of purine itself. But, for the sake of convenience, only the formulae of the type I are usually employed.

The **hydroxy derivatives** of purine are derived by the substitution of OH groups for the hydrogen of the three CH groups at positions 2, 6 and 8 of the purine molecule, and are assigned tautotumeric formulae (*a*) and (*b*) as given below for xanthine (2, 6-dihydroxypurine) :—


(*a*) Lactam form

⇌


(*b*) Lactim form

Similarly, other hydroxy derivatives of purine exist in the keto or lactam and the enol or lactim forms, but, for the sake of convenience, only the lactam formulae are usually employed.

The **amino derivatives** are likewise derived by the replacement of the hydrogen of the CH groups by the NH_2 groups. The **methyl derivatives,** on the other hand, are derived by the substitution of methyl groups for the hydrogen of the NH groups of the lactam form of a hydroxypurine.

6. Uric Acid, *2,6,8,-Trihydroxypurine*, $C_5N_4H_4O_3$.—

Occurrence. While urea represents the principal nitrogenous end-product of human and mammalian food, some uric acid is also produced, and is excreted in the urine in the form of sodium and potassium salts. In the case of birds, snakes and lizards it is the uric acid that is the main component of the excreta.

Preparation. Uric acid is obtained on a commercial scale (for use in the manufacture of caffein) from the excrement of sea birds (*guano*), which consists principally of ammonium urate and huge deposits of which are available in South Sea Islands and elsewhere near the sea. The guano is boiled with aqueous sodium hydroxide, until all ammonia has been expelled. The liquid, while still hot, is filtered and acidified with hydrochloric acid. On allowing to stand, uric acid separates as a fine, crystalline powder.

---

[1] This, of course, is not the case with those derivatives which contain oxygen in the *five*-membered ring (*e.g.* uric acid).

Physical Properties. Uric acid is a colourless, crystalline powder, without any taste or smell. The crystals may be of various shapes, depending upon the rate of crystallization from solution, but usually they consist of rhombic plates or prisms, sometimes arranged in sheaves (Fig. 1). Uric acid is only slightly soluble in hot water, and practically insoluble in cold. It is insoluble in alcohol and ether, but soluble in glycerol. It also dissolves in cold concentrated sulphuric acid, from which it is precipitated on dilution with water.

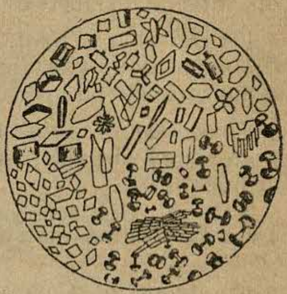
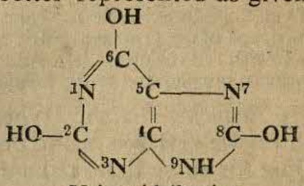


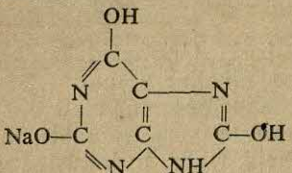
Fig. 1.
Crystals of uric acid as seen under the microscope.

Reactions of Uric acid :—

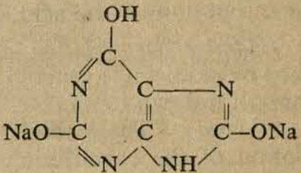
(1) *Acidic Nature.* Uric acid gives two series of salts (primary and secondary) derived from the enolic form, which is better represented as given in the margin to bring out its **phenolic character.** The grouping $N=C-OH$ of the uric acid molecule is analogous to the $O=C-OH$ grouping of carboxylic acids and to the grouping $C=C-OH$ present in enols and phenols. Blitz and Hermann have shown that the hydrogen at position 2 is the one most easily replaced and that at position 8 comes next. So, we have :—



Uric acid (lactim or phenolic form)



Monosodium urate



Disodium urate

Salts of uric acid (even those of the alkali metals) are very sparingly soluble in water. The primary lithium salt is most soluble (one part in 400). For this reason, "lithia water" was formerly employed by gouty patients as a solvent for uric acid. This view has been found to be incorrect, and the practice of using lithia water has, therefore, been discontinued.

(2) *Action of Phosphorus Oxychloride.* This reagent, too, reacts with the *enolic* form of uric and replaces the OH groups by chlorine.* First, we get 2,6-dichloro-8-hydroxypurine and then 2,6,8-trichloropurine. These compounds have been employed for the synthesis of a large number of purine derivatives from comparatively cheap uric acid. The chlorine atom can be readily replaced by the groups, $-OC_2H_5$, $-OH$, $-SH$, $-NH_2$, -1, and also partially by $-H$. By

this means not only has it been possible to synthesize the few naturally-occurring purine derivatives, but also a very large number of synthetic members of this group have been prepared.

(3) *Action of Heat.* When uric acid is heated, it undergoes decomposition with the formation of urea, ammonium carbonate, cyanuric acid and hydrogen cyanide ; and a charred mass remains.

(4) *Action of Solid KOH.* When uric acid is heated with solid potassium hydroxide, ammonia is evolved and a residue of potassium cyanide is left.

Expt. 1. Heat some uric acid with a piece of solid potassium hydroxide. Test the evolved gas with a moist red litmus paper, and the residue in the tube for cyanide.

(5) *Action of Concentrated Sulphuric Acid.* When uric acid is heated with concentrated sulphuric acid, it undergoes charring.

(6) **Murexide Test.** This is the most characteristic test of uric acid, and is carried out as in the following experiment.

Expt. 2. Murexide Test. Take a small quantity of uric acid in a dish, add a few drops of concentrated nitric acid and evaporate to dryness on a water bath. A yellowish red residue is left. Add a drop of ammonia with a glass rod, the colour changes to purple, due to the formation of *murexide* (ammonium purpurate).

(7) *Reducing Action.* When a solution of uric acid is warmed with **Fehling's solution,** white precipitate of copper urate is formed. On boiling for some time, reduction of the Fehling's solution occurs with precipitation of cuprous oxide.

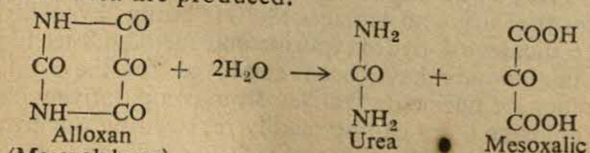
Uric acid reduces alkaline silver nitrate, a black precipitate of metallic silver being formed. It also decolorises acidified potassium permanganate. The reaction forms the basis of Hopkin's method for the estimation of uric acid.

(8) *Oxidative Degradation of Uric Acid.* Uric acid is readily attacked by oxidizing agents in acid and alkaline solutions. Nitric acid breaks it down to *alloxan*, while alkaline permanganate converts it into *allantoin*. These results have proved very valuable in the elucidation of the constitution of uric acid, which is discussed in the following section.

7. Constitution of Uric Acid.—The constitution of uric acid follows from the following considerations.

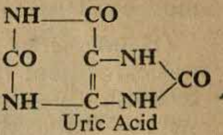
(1) The molecular formula of uric acid is $C_5N_4H_4O_3$.

(2) When carefully oxidized with nitric acid, uric acid yields alloxan and urea. The constitution of urea is already known ; that of alloxan follows from its hydrolysis with alkalis, when mesoxalic acid and urea are produced.

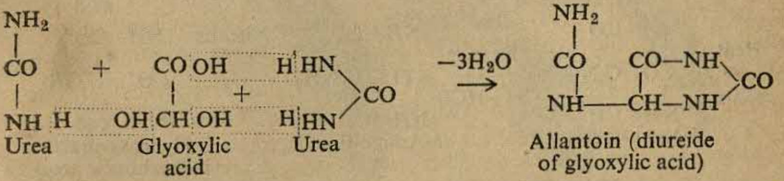


Alloxan (Mesoxalylurea) Urea Mesoxalic acid

Uric acid, therefore, appears to be a **diureide** containing in its molecule, the *skeleton of mesoxalylurea and another ring having a urea linkage*. The presence of four nitrogen atoms in the molecular formula is in accord with this view. So, we may tentatively write the structural formula of uric acid as shown in the margin. This formula, first suggested by Medicus in 1875, is fully supported by other facts as detailed below.



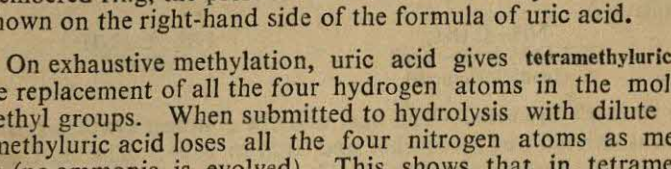
(3) Oxidation of uric acid with potassium permanganate in alkaline solution gives **allantoin** as the main product. The structure of allantoin follows from its synthesis by heating glyoxylic acid, $CHO.COOH\ H_2O$, or $CH(OH)_2.COOH$, with urea :—



This proves the presence of a five-membered ring (in addition to the six-membered ring, the presence of which has already been established) shown on the right-hand side of the formula of uric acid.

(4) On exhaustive methylation, uric acid gives **tetramethyluric acid** by the replacement of all the four hydrogen atoms in the molecule by methyl groups. When submitted to hydrolysis with dilute HCl, tetramethyluric acid loses all the four nitrogen atoms as methylamine (no ammonia is evolved). This shows that in tetramethyluric acid all the methyl groups are directly linked to nitrogen. Hence, all the four hydrogen atoms of the uric acid molecule must be attached to nitrogen, which is in agreement with the formula given above.

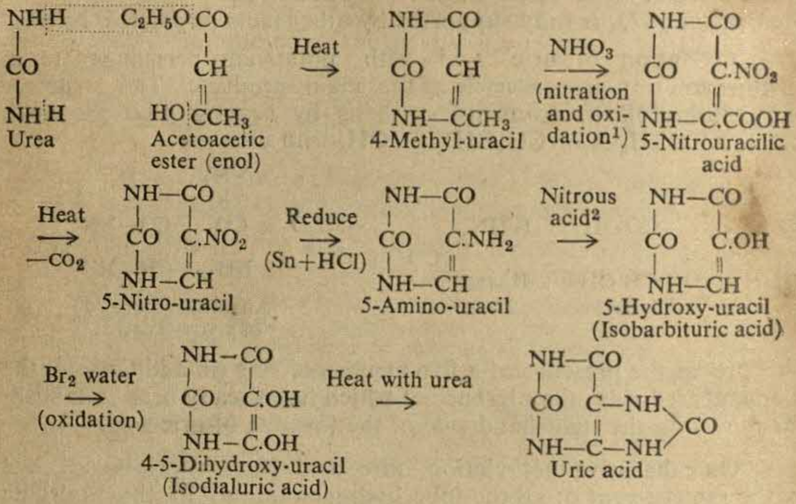
8. Tautomerism of Uric Acid.—While the evidence put forward in the foregoing section supports the keto- or lactam-formula of uric acid, its acidic nature and behaviour towards phosphorus oxychloride (reactions 1 and 2 given in sec. 6) clearly prove that the molecule contains three hydroxyl groups. Hence, uric acid is supposed to exist in **two tautomeric forms** in equilibrium :—



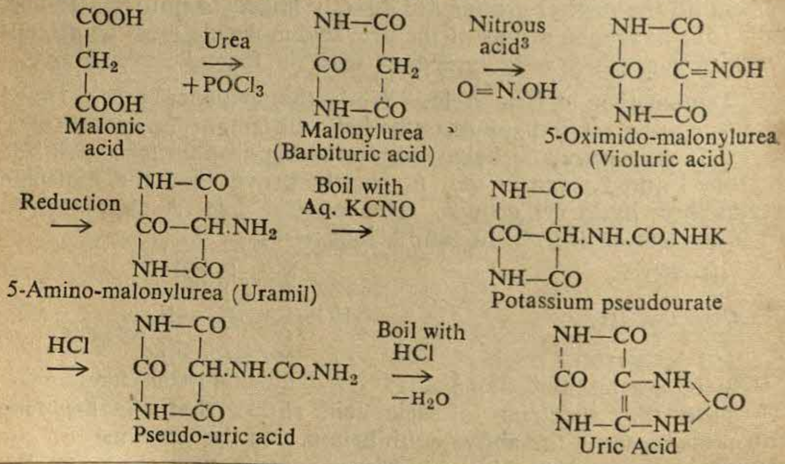
The absorption spectrum of uric acid shows that the **keto-form greatly predominates** in the above equilibrium. In the presence of the hydroxyl group reagents, the equilibrium continuously shifts to the right.

9. Syntheses of Uric Acid.—As stated above, the structural formula of uric acid was put forward by Medicus in 1875 before sufficient evidence was available to prove it beyond doubt. The formula was later confirmed by the following syntheses.

(1) **Behrend and Roosen's Synthesis.** The first synthesis of uric acid was carried out by Behrend and Roosen in 1888, and served to establish the constitution of uric acid on a firm footing. The various steps of this synthesis are :



(2) **Fischer's Synthesis.**—The next and the simplest synthesis of uric acid was carried out by Fischer and Ach in 1895. The starting substance in this case was malonic acid :—



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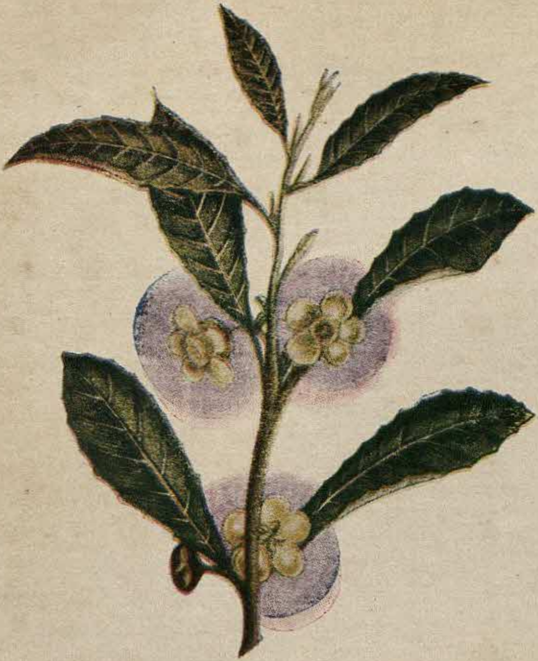
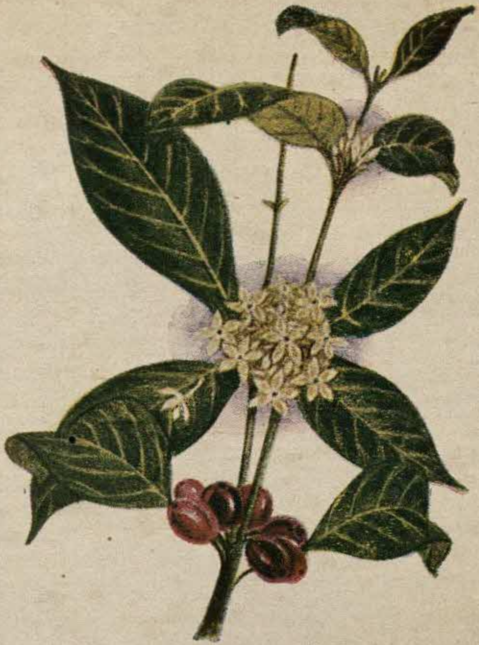
[1] The action of nitric acid, nitration and oxidation of the alkyl group to COOH group, is suggestive of the *aromatic* nature of the six-membered ring of uracil.

[2] Compare the action of nitrous acid on primary amines.

[3] Compare action of nitrous acid on primary nitroparaffins.



Camellia thea



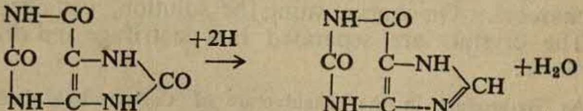
Coffea arabica

[*To face page 481*]

As violuric acid is the oxime of alloxan, the chief oxidation product of uric acid, this synthesis permits the reconstruction of uric acid after its oxidative break-down to alloxan.

10. Xanthine, *2,6-Dihydroxypurine.*—This important substance occurs in the urine, blood, liver and urinary calculi. Small quantities of xanthine accompany caffeine in tea.

Xanthine is readily obtained by the reduction of uric acid with sodium amalgam :—

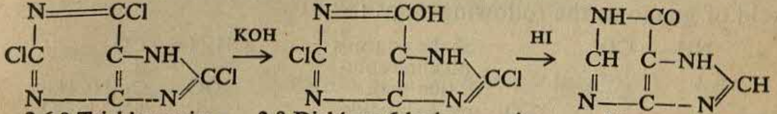


Uric acid Xanthine

Like other hydroxy derivatives of purine, xanthine exhibits tautomerism.

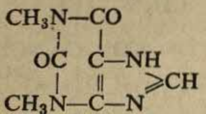
Xanthine crystallizes readily, and, like uric acid, is very sparingly soluble in water. It forms salts with alkalis, and also yields a hydrochloride and a nitrate. It gives the murexide reaction.

11. Hypoxanthine (*6-Hydroxypurine*).—This purine derivative is widely distributed in plants and animals. It may be conveniently prepared from 2,6,8-trichloropurine :—



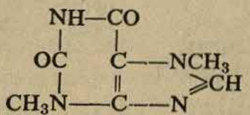
2,6,8-Trichlorpurine 2,8-Dichloro-6-hydroxypurine Hypoxanthine

12. Methylxanthines.—Of the five naturally occurring methylxanthines, the more important are :—



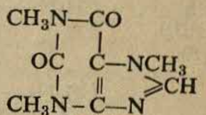
Theophylline

(1,3-Dimethylxanthine)



Theobromine

(3,7-Dimethylxanthine)



Caffeine

(1,3,7-Trimethylxanthine)

All these three occur in nature, and are used in medicine as diuretics.

13. Caffeine, or **Theine.**—This is the most important of the methylxanthines. It is the principal alkaloidal constituent of tea, coffee and some other beverages, in which it occurs either free or combined as caffein chlorogenate. The following are the percentages present in different materials :—

Tea,	1 to 4·5 per cent	Kola nuts,	2·5 to 3·5 per cent
Coffee,	1 to 1·5 per cent	Cocoa beans,	1 to 2 per cent

Manufacture of Caffeine.—

(1) **From Tea Waste.** Caffeine is manufactured in India from tea dust coming from tea gardens of Darjeeling, Assam, Terai and Dooars. The raw material, mixed with sodium carbonate and water, is placed in brass extractors fitted with condensers and working on the Soxhlet principle, and is submitted to extraction with benzol

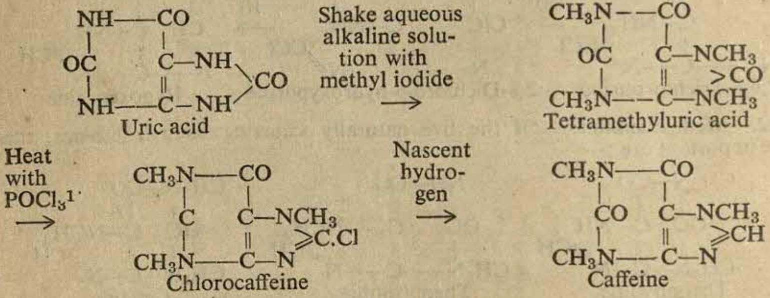
(boiling range 70° to 100°). When the extraction has been completed, the solvent is distilled off and reused.

The solid residue is extracted with water, and the extract is treated with basic lead acetate to precipitate chlorophyll, resin, wax and gums. The precipitate is filtered off, and the filtrate is treated with hydrogen sulphide (or sulphuric acid) to eliminate lead. After filtering off lead sulphide (or sulphate), the filtrate is decolorized with activated charcoal. On concentrating the solution, caffeine crystallizes out. The crystals are separated in a centrifuge and dried at room temperature.

(2) **As By-product in the manufacture of Caffeine-free Coffee.** Coffee beans are treated with superheated steam, and the caffeine extracted with benzol as described above.

(3) **From Cocoa Waste.** Large quantities of caffeine are manufactured in America by the methylation of theobromine, the latter being obtained from the residual cocoa-cake after the "oil of theobroma" has been extracted.

(4) **From Uric Acid.** Some caffeine is also manufactured from uric acid of guano in the following steps :—



Properties of Caffeine.—

(1) Caffeine crystallizes from water in long, silky needles containing one molecule of water. When heated, the crystals lose their water content at 100° ; on further heating, the substance melts at 234°. It can be sublimed unchanged at 175°.

(2) Caffeine is readily soluble in water or chloroform, fairly soluble in alcohol or benzene, and sparingly soluble in ether or carbon tetrachloride.

(3) Caffeine is a feeble base with a bitter taste, and forms salts which are readily hydrolysed by water. For this reason, it is left unchanged by boiling, concentrated hydrochloric acid.

(4) When warmed with potassium ferrocyanide and nitric acid, it produces a precipitate of Prussian blue.

---

[1] In this reaction methyl group in position 9 gets detached, and the oxygen atom in position 8 becomes replaced by chlorine :

$$3C_5O_3.N_4(CH_3)_4 + POCl_3 \rightarrow 3C_5ON_4(CH_3)_3Cl + PO(OCH_3)_3$$

Physiological Action. Caffeine exerts a stimulating action on the heart and the higher psychic centres of the brain. It is used in medicine for these purposes and also as a diuretic. The use of tea and coffee as a drink produces the same effects.

Tests for Caffeine. (1) Evaporate a minute quantity of caffeine with concentrated nitric acid; a yellow residue is left, which, on the addition of ammonia, becomes intensely purple (murexide test)[1].

(2) Evaporate a solution of caffeine in chlorine water; a yellowish brown residue is left which on the addition of dilute ammonia yields a violet red solution.

Uses.—

(1) In medicine (see under Physiological Action).

(2) Large quantities of caffeine are used, particularly in U.S.A., for the preparation of **Cola type soft drinks** of which caffeine is an essential constituent.

14. Theobromine. *3,7-Dimethylxanthine.*—Theobromine occurs in cocoa beans (*Theobroma cacoa*). It is a crystalline powder with a bitter taste, and forms salts with alkalis as well as acids. When treated with an ammoniacal solution of silver oxide, it gives a silver salt, which reacts readily with methyl iodide yielding caffeine.

Uses.—

(1) Like caffeine, theobromine is used in medicine.

(2) Large quantities are employed in America in the manufacture of caffeine.

QUESTIONS

1. What are cyclic ureides and purines? Describe the relation, if any, that exists between them, and their importance.

2. Describe the preparation and uses of veronal. (*Bombay, B.Sc., 1953*)

3. How does uric acid occur in nature? How would you isolate it and establish its constitution? What relationship exists between uric acid, xanthine and caffeine? (*Panjab, B.Sc., 1949*)

4. How has the constitution of uric acid been determined? Describe any one synthesis of uric acid. Write down the formulae of Xanthine and Caffeine. (*Panjab, B.Sc., 1946*)

5. Discus the structure of uric acid, giving at least one synthesis. How can you convert uric acid into caffeine? (*Delhi, B.Sc., 1951*)

6. How is uric acid synthesized? Show its relationship to purine, caffeine and theobromine. (*Bombay, B.Sc., 1951*)

7. Discuss the constitution of uric acid both analytically and synthetically. How are uric acid, caffeine and theobromine related to each other? (*Poona, B.Sc., 1954*)

8. How may caffeine be prepared from (*a*) tea leaves, (*b*) uric acid? Give its important properties and tests. (*Panjab, B.Sc., 1937*)

9. Give the occurrence, chief properties and use of *theobromine.*

10. Describe what are ureides and give examples. (*Rajasthan, B.Sc., 1961*)

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[1] This test is also given by uric acid.

11. Discuss the constitution of uric acid and describe one of its syntheses. Show its relationship to caffeine and theobromine. *(Bombay, B.Sc., 1941)*

12. How is uric acid synthesised ? Show its relationship to purine, caffeine and theobromine. *(Bombay, B.Sc., 1951)*

13. Discuss the constitution of uric acid. Show its relationship with caffeine, theobromine and purine. *(Gujarat, B.Sc., 1956)*

14. What is uric acid ? How is it obtained from the urine in pure condition ? Describe some important chemical properties of uric acid. *(Calcutta, First M.B.B S., 1955)*

15. What do you know of the structure of uric acid and how do you account for its acidity ? *(Calcutta, First M.B.B.S., 1960)*

16. Describe the source, preparation and properties (including solubility) of uric acid. Give the structural formula of uric acid and discuss its basicity. *(Calcutta, First M.B.B.S., 1959)*

17. Give the synthesis of uric acid. *(Baroda, B.Sc., 1954)*

18. How is veronal prepared ? Mention its important uses, *(Patna, B.Sc., 1958)*

19. Give analytical and synthetical evidence to prove the structure of Uric acid and show how it is related to Caffeine and Theobromine. *(Poona, B.Sc., 1958)*

20. Discuss the structure of Uric acid. How is it related to Xanthine and Caffeine? *(Lahore, B.Sc., 1958)*

21. How is Caffeine prepared ? Describe its important properties and uses. *(Panjab, B.Sc., 1959)*

22. Give a synthesis of Uric acid and indicate how caffeine and theobromine are related to it. *(Karnatak, B.Sc., 1960)*

23. Discuss the constitution of Uric acid. Give its synthesis from urea and ethyl cyanoacetate. Show the interrelationship that exists amongst the members of the purine group. *(Vallabhbhai, B.Sc., 1961)*

24. Discuss fully the constitution of Uric acid. *(Patna B.Sc.. 1961)*

CHAPTER THIRTY-FOUR

CARBOHYDRATES

1. **General.**—*The group of organic substances that have the characteristic of sugars, or resemble them in structure and chemical behaviour, are termed* **carbohydrates.** The name was originally based on the fact that all the substances of this class, then known, could be represented by the general empirical formula $Cx(H_2O)y$. So, it was thought that these compounds were the "hydrates of carbon" or "carbohydrates." The basis of this term has now disappeared, as quite a number of substances having the characteristics of carbohydrates do *not* possess the above empirical formula.

On the other hand, there exist compounds (*e.g.*, formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$) that have this empirical formula, but do *not* at all possess the characteristics of carbohydrates. The term "carbohydrates" is retained on account of long use and convenience, but its significance has altogether changed.

2. **Classification of Carbohydrates.**—Carbohydrates are classified systematically as follows:

(1) The **monosaccharides**, which are the simplest, non-hydrolysable members, such as *glucose* and *fructose*.

(2) The **oligosaccharides** (Gr. *oligos*, few), which are simpler polysaccharides, and, on hydrolysis, give two, three or four monosaccharide molecules, Sucrose (cane sugar) maltose (malt sugar) and lactose (milk sugar) are typical members of this class. Oligosaccharides are subdivided into **disaccharides, trisaccharides** and **tetrasaccharides**, according to the number of monosaccharide units going into their structure.

(3) The **polysaccharides** are also condensation products of monosaccharides, but their molecules consist of a *very large* number of monosaccharide units. They are either altogether insoluble in water *e.g.*, cellulose or, at best, form colloidal sols. (*e.g.*, starch and glycogen).

2. MONOSACCHARIDES

3. **Classification of Monosaccharides.**—Monosaccharides fall into two divisions according to their structure: (1) **aldoses**, which are polyhydroxyaldehydes, and (2) **Ketoses** which are polyhydroxyketones. Glucose, $CH_2OH(CHOH)_4CHO$, is the most important example of an aldose, and fructose, $CH_2OH(CHOH)_3COCH_2OH$, that of a ketose. A further distinction is drawn according to the *number of oxygen-carrying*[1] *carbon atoms* present in the molecule. Thus, we have **trioses, tetroses, pentoses, hexoses**, etc. Fructose, for example, is a ketohexose, and arabinose an aldopentose.

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[1] Thus, $CH_3(CHOH)_4CHO$ is not a hexose but a methylpentose.

The number of monosachharides known at present is about fifty, of which ten have been found to occur in nature. The rest have been prepared synthetically by methods which could be employed to synthesize hundreds of other members of this group. The existence of such a vast number of monosaccharides is due to the presence of asymmetric carbon atoms in their molecules. Thus, aldopentoses, $CH_2OH(CHOH)_3CHO$, and ketohexoses, $CH_2OH(CHOH)_3COCH_2OH$, which contain 3 asymmetric carbon atoms in their molecules, exist in 2^3 or 8 forms, while aldohexoses, $CH_2OH(CHOH)_4CHO$, which contain four asymmetric carbon atoms, exist in 2^4 or 16 forms, But actually the number is much larger on account of *tautomarism* which plays an important part in the case of sugars.

4. Occurrence and Sources of Monosaccharides.—

1. Glucose and fructose are the two monosaccharides that occur as such in nature, and are found abundantly in sweet fruits.

2. Much larger quantities of monosaccharides occur as component units of the molecules of oligosaccharides (*e.g.*, sucrose and lactose) and polysaccharides (*e.g.*, starch and cellulose), from which sources they are obtained by hydrolysis.

3. Another important source of monosaccharides is the **glycosides**, *i.e.*, the compounds of monosaccharides with other substances (such as alcohols and phenols).

5. Physical Properties of Monosaccharides.—

1. Monosaccharides are sweet tasting, water-soluble, neutral substances. They are sparingly soluble in alcohol and practically insoluble in ether and hydrocarbons. On heating, they first turn brown (caramelized) and then get charred, emitting characteristic, burnt-sugar odour.

2. They are optically active, possessing, in each case, a definite *specific rotation*. This constant is of special importance and not only serves to characterize a given sugar but also to estimate its concentration in solution.

3. The rotation of an aqueous solution of a monosaccharide changes on standing. It gradually increases, or decreases, and finally acquires a definite, constant value. The phenomenon is called *mutarotation*, and is described later.

6. General Reactions of Monosaccharides and their Open-chain Structure.—Many of the important chemical reactions of monosaccharides are explained by the **open-chain formulae** assigned to them in earlier systematic study of sugars, notably by Fischer and Kiliani. The formulae for the two most important monosaccharides, glucose and fructose, are given below :

$$\overset{6}{C}H_2OH.\overset{5}{C}HOH.\overset{4}{C}HOH.\overset{3}{C}HOH.\overset{2}{C}HOH.\overset{1}{C}HO$$

Glucose (a typical aldose)

$$\overset{6}{C}H_2OH.\overset{5}{C}HOH.\overset{4}{C}HOH.\overset{3}{C}HOH.\overset{2}{C}O.\overset{1}{C}H_2OH$$

Fructose (a typical ketose)

The **numbering of the carbon atoms** in the chain is in accordance with the I.U.C. system for aldehydes (for aldoses) and ketones (for ketoses).

Glucose, as seen from its formula, is an **aldohexose**, *i.e.*, a six-carbon sugar with an aldehyde group in the molecule. Fructose is a **2-ketohexose**, because the molecule consists of a 6-carbon chain with a keto group at position 2. The chemical evidence that led to the adoption of these formulae is as follows:—

(1) **Acetylation.** When heated with acetic anhydride and a little zinc chloride, glucose and fructose both give **crystalline penta-acetates**; showing the existence of five OH groups in the molecule of each.

$$\underset{\text{Glucose pentaacetate}}{CH_2OAc(CHOAc)_4CHO} \qquad \underset{\text{Fructose pentaacetate}}{CH_2OAc(CHOAc)_3COCH_2OAc}$$

Similarly, the number of hydroxyl groups in the molecule of any other sugar can be determined.

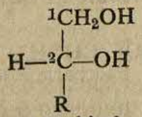
NOTE. The **symbol Ac** stands for the **acetyl group**, $CH_3CO—$

(2) **Reduction.** On reduction with sodium amalgam, monosaccharides take up two atoms of hydrogen at the carbonyl group, and form polyhydric alcohols. Thus, glucose and fructose give hexahydric alcohols ; the former gives sorbitol and the latter a mixture of sorbitol and mannitol.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 2H \rightarrow \underset{\text{Sorbitol}}{CH_2OH(CHOH)_4CH_2OH}$$

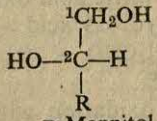
$$\underset{\text{Fructose}}{CH_2OH(CHOH)_3COCH_2OH} + 2H \rightarrow \underset{\text{Sorbitol and Mannitol}}{CH_2OH(CHOH)_4CH_2OH}$$

Sorbitol and mannitol are **optical isomers** differing in the configurational disposition of the CHOH group at position 2. Representing by R the part $CH_2OH(CHOH)_3—$of the molecule (which is identical in both cases), the two hexahydric alcohols are represented as follows :—



$$\begin{array}{c} {}^{1}CH_2OH \\ | \\ H—{}^{2}C—OH \\ | \\ R \end{array}$$

D-Sarbitol



$$\begin{array}{c} {}^{1}CH_2OH \\ | \\ HO—{}^{2}C—H \\ | \\ R \end{array}$$

D-Mannitol

(3) **Addition of HCN.** Kiliani, in 1886, discovered that monosaccharides add on a molecule of hydrogen cyanide to form cyanohydrins, a fact that established the presence of a **carbonyl group** in the sugar molecule.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + HCN \rightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH(CHOH)_4CH(OH)CN}$$

$$\underset{\text{Fructose}}{CH_2OH(CHOH)_3COCH_2OH} + HCN \rightarrow \underset{\text{Fructose cyanohydrin}}{CH_2OH(CHOH)_3C(OH)CN.CH_2OH}$$

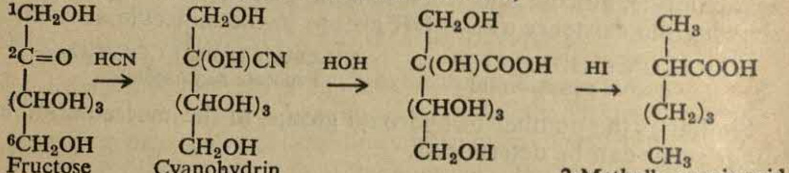
(4) **Hydrolysis of Cyanohydrins.** Kiliani hydrolysed glucose cyanohydrin and submitted the resulting acid to reduction by

hydrioic acid, when he got **normal heptanoic acid** by the replacement of all OH groups by hydrogen.

$$\underset{\text{Glucose cyanohydrin}}{CH_2OH(CHOH)_5CN} \xrightarrow{\text{HOH}} \underset{\text{Hexahydroxyheptanoic acid}}{CH_2OH(CHOH)_5COOH} \xrightarrow{\text{HI}} \underset{\text{Heptanoic acid}}{CH_3(CH_2)_5COOH}$$

The result proved that the glucose molecule consists of a **straight chain of carbon atoms** and that the carbonyl group is a terminal —CHO group.

Fructose cyanohydrin, on being hydrolysed followed by reduction of the product by HI, give **2-methylhexanoic acid,**



Fructose Cyanohydrin 2-Methylhexanoic acid

From this observation, Kiliani deduced that fructose is a pentahydroxy ketone with the carbonyl group at position-2 of the *normal*-hexane chain.

Kiliani's method has been employed in **determining the nature of chain** in all the known natural sugars, and it has been found that, with very few exceptions, they all possess a straight chain of carbon atoms.

(5) **Oxidation.** Kiliani's conclusion as to the structure of monosaccharides is confirmed by their behaviour on oxidation. Aldoses, when oxidized with mild oxidizing agents (*e.g.*, silver salts or bromine water) give monocarboxylic hydroxy-acids, called **aldonic acids**, having the *same number of carbon atoms* as the aldose itself.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{+O} \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH}$$

Concentrated nitric acid oxidizes the molecule at both ends, giving a dicarboxylic hydroxy acid :—

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 3O \longrightarrow \underset{\text{Saccharic acid}}{HOOC(CHOH)_4COOH} + H_2O$$

Ketoses, on oxidation with nitric acid, undergo a cleavage of the molecule at the CO group and give *acids with a smaller number of carbon atoms* ; *e.g.*

$$\underset{\text{Fructose}}{CH_2OH(CHOH)_3COCH_2OH} \rightarrow \underset{\text{Tartaric acid}}{HOOC(CHOH)_2COOH} + \underset{\text{Glycolic acid}}{HOOC.CH_2OH}$$

(6) **Formation of oximes.** By virtue of the presence of the carbonyl group in the molecule, monosaccharides react with hydroxylamine to form oximes (compare aldehydes and ketones) :—

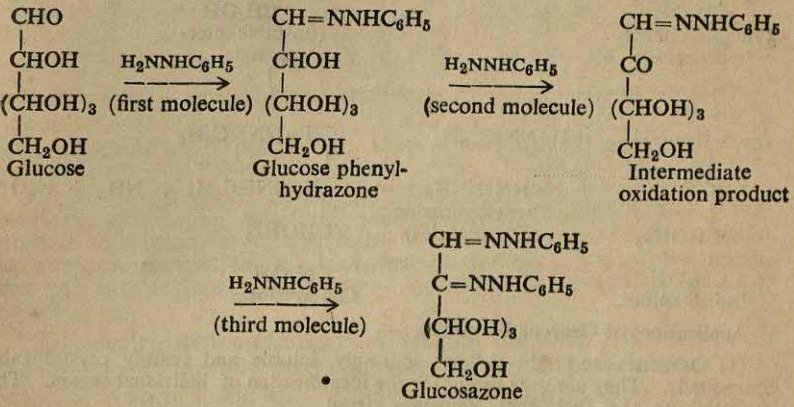
$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{NH_2OH} \underset{\text{Glucose oxime}}{CH_2OH(CHOH)_4CH{=}NOH}$$

$$\underset{\text{Fructose}}{CH_2OH(CHOH)_3COCH_2OH} \xrightarrow{NH_2OH} \underset{\text{Fructose oxime}}{CH_2OH(CHOH)_3C({=}NOH)CH_2OH}$$

(7) **Osazone formation.** One of the outstanding contributions of Fischer (1884) in the study of sugars was the use of phenylhydrazine, a reagent that was known to give, with aldehydes and ketones, sparingly soluble, crystalline derivatives called *phenylhydrazones.* The reaction of phenylhydrazine with sugars gave unexpected results. The products, to which he gave the name **osazones** (*-ose+hydrazone*), contained two phenylhydrazine residues instead of one.

Another interesting observation was that fructose gave the same osazone as glucose, *i.e.* glucosazone. The other two hexoses known at the time (galactose and sorbose), however, gave their own respective osazones.

In 1887, Fischer was able to isolate the true phenylhydrazone of glucose, which on further treatment with phenylhydrazine gave glucosazone. Thus, he proved that phenylhydrazone was the intermediate in osazone formation, and on this basis he suggested the following course of the reaction :—



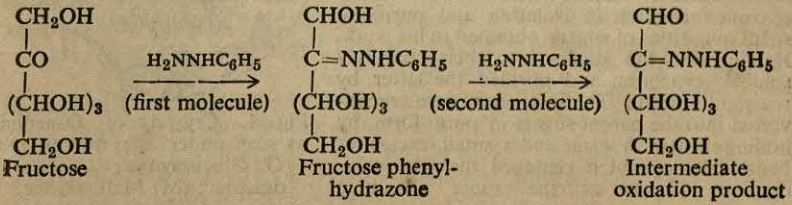
$$\begin{array}{c}\mathrm{CHO}\\|\\\mathrm{CHOH}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Glucose}\end{array}\xrightarrow[\text{(first molecule)}]{H_2NNHC_6H_5}\begin{array}{c}\mathrm{CH{=}NNHC_6H_5}\\|\\\mathrm{CHOH}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Glucose phenyl-}\\\text{hydrazone}\end{array}\xrightarrow[\text{(second molecule)}]{H_2NNHC_6H_5}\begin{array}{c}\mathrm{CH{=}NNHC_6H_5}\\|\\\mathrm{CO}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Intermediate}\\\text{oxidation product}\end{array}$$

$$\xrightarrow[\text{(third molecule)}]{H_2NNHC_6H_5}\begin{array}{c}\mathrm{CH{=}NNHC_6H_5}\\|\\\mathrm{C{=}NNHC_6H_5}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Glucosazone}\end{array}$$

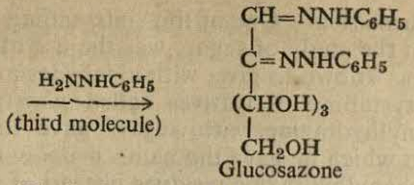
Out of the three molecules of phenylhydrazine taking part in the reaction, the first and the third react in the normal manner, while the second was assumed to oxidize the CHOH group at position-2 to a CO group, being itself reduced to ammonia and aniline.

$$-\mathrm{CHOH}- + H_2NNHC_6H_5 \longrightarrow -\mathrm{CO}- + NH_3 + C_6H_5NH_2$$

Similarly, the reaction with fructose to give glucosazone was assumed to proceed as follows :

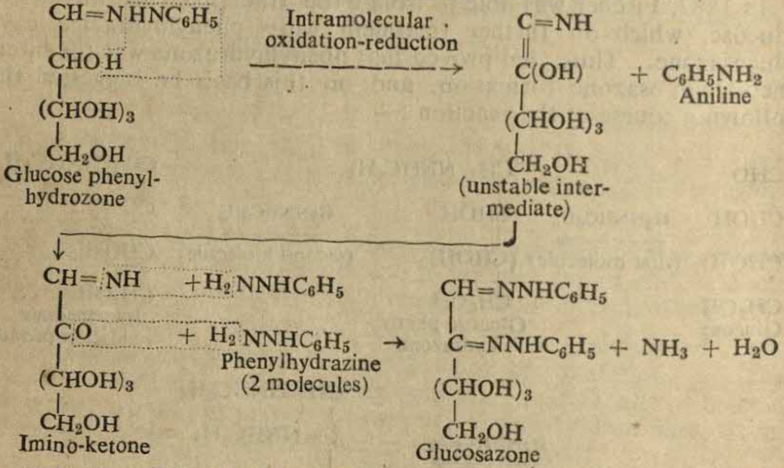


$$\begin{array}{c}\mathrm{CH_2OH}\\|\\\mathrm{CO}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Fructose}\end{array}\xrightarrow[\text{(first molecule)}]{H_2NNHC_6H_5}\begin{array}{c}\mathrm{CHOH}\\|\\\mathrm{C{=}NNHC_6H_5}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Fructose phenyl-}\\\text{hydrazone}\end{array}\xrightarrow[\text{(second molecule)}]{H_2NNHC_6H_5}\begin{array}{c}\mathrm{CHO}\\|\\\mathrm{C{=}NNHC_6H_5}\\|\\(\mathrm{CHOH})_3\\|\\\mathrm{CH_2OH}\\\text{Intermediate}\\\text{oxidation product}\end{array}$$



$$\xrightarrow[\text{(third molecule)}]{H_2NNHC_6H_5} \begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

Modern View. Fischer's view of the second phase of the reaction became questionable when it was realized that phenylhydrazine fails to oxidize such a powerful reducing agent as titanous chloride. So, Weygand, in 1940, put forward an alternative view, according to which the simultaneous formation of aniline and the osazone is due to an **intramolecular oxidation-reduction reaction** as shown below :—



$$\begin{array}{l} CH{=}NHNC_6H_5 \\ | \\ CHOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \xrightarrow{\text{Intramolecular oxidation-reduction}} \begin{array}{l} C{=}NH \\ \| \\ C(OH) \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + C_6H_5NH_2$$

$$\begin{array}{l} CH{=}NH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \begin{array}{l} +H_2NNHC_6H_5 \\ \\ +H_2NNHC_6H_5 \end{array} \rightarrow \begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + NH_3 + H_2O$$

Applications of Osazone Formation :—

(1) Osazones are bright yellow, sparingly soluble and readily crystallizable compounds. They are very useful for the **identification of individual sugars.** This is based on the fact that osazones from different sugars are of different crystalline forms and tend to cluster together in different ways which can easily be recognized under the microscope (Fig. 1.).

(2) Another very important use of osazone formation is in the **purification of sugars** in researchwork. One of the chief difficulties in the earlier work on sugars lay in their very high water-solubility and tendency to form syrups, from which they could not be separated by crystallization. Fischer made extensive use of osazone formation in isolating and purifying small quantities of sugars obtained in his work. He converted the sugars into their sparingly soluble osazones, and purified the latter by recrystallization. The osazones were reconverted into the parent sugars in pure form by boiling them with water and a small excess of benzaldehyde, which removed the phenylhydrazine radicals as the more insoluble

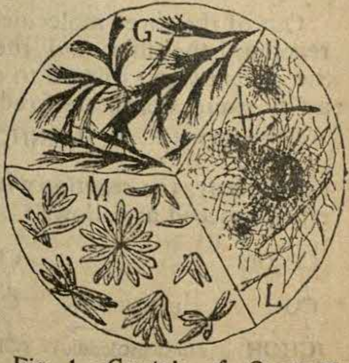
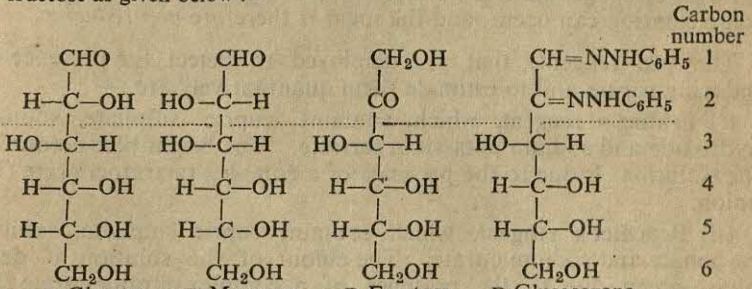


Fig. 1. Crystals of Osazones as seen under the microscope. (G) Glucosazone ; (L) Lactosazone ; (M) Maltosazone.

phenylhydrazone of benzaldehyde. The latter was filtered off, and the filtrate, consisting of an aqueous solution of the sugar, concentrated to crystallization in a vacuum desiccator.

(3) A third use of osazone formation is the **conversion of aldoses into ketoses** (sec. 11, p. 495).

(4) Osazone formation has also been utilised in **establishing configurational relationships** of sugars. Since the formation of osazone concerns only the carbon atoms 1 and 2, if two or more monosaccharides give the same osazone, it follows that they have exactly the same configuration so far as the asymmetric carbon atoms 3, 4 and 5 are concerned and that the difference lies only in the configuration of asymmetric carbon atom 2 of the chain. To take a specific example, D-glucose, D-mannose and D-fructose give the same osazone (namely glucosazone), and D-glucose has been shown to have the configuration given below on independent grounds. Hence we deduce the configurations of D-mannose and D-fructose as given below :—



D-Glucose D-Mannose D-Fructose D-Glucasazone

As seen in the above scheme, the configuration below the dotted line is identical in all the cases. Since D-mannose is an aldohexose like D-glucose itself and since the configuration of asymmetric carbon atom 2 in glucose is known, that in D-mannose must have the alternative arrangement. In D-fructose, carbon atom number 2 is not asymmetric, and so the question of its configuration does not arise.

(8) **Reducing Action of Sugars in Alkaline Solution.** The behaviour of monosaccharides towards oxidising agents, where the oxidation proceeds in accordance with definite chemical equations, has already been described (Reaction 5, page 488).

All monosaccharides and disaccharides (excepting sucrose) reduce certain oxidizing agents in *alkaline* solution. Thus, cupric compounds are reduced by reducing sugars to cuprous oxide, silver compounds to metallic silver and ferricyanides to ferrocyanides. A peculiarity of alkaline-reducing action of sugars is that the reaction does not occur in accordance with any definite stoichiometric equation. Thus, the weight of cuprous oxide precipitated by glucose from an alkaline cupric solution is *between two and three times* the amount calculated from the equation :

$$\underset{\text{Glucose}}{RCHO} + 2\,Cu(OH)_2 \longrightarrow \underset{\text{Gluconic acid}}{RCOOH} + Cu_2O + 2H_2O$$

In all these reactions we have to adhere strictly to the experimental conditions laid down by previous workers, especially in quantitative estimations. An **empirical factor** must be used for each reagent and each sugar. Thus, 10.0 ml. of Benedict's quantitative reagent are reduced by 20·0 milligrams of glucose.

The cause of reducing action of sugar obviously does not lie in the mere presence of the readily oxidizable —CHO group, for, had it been so, it would be possible to represent the reaction stoichiometrically by a chemical equation. Another important point that leads to the same conclusion is that **ketoses reduce as well as aldoses.** On the other hand, sugars (*e.g.*, sucrose) that contain no carbonyl group at all are **non-reducing.** Careful study of the problem has shown that the real cause lies in the rupture of carbon chains, giving **highly reactive fragments** containing one to five carbon atoms. Hence, reducing power of a sugar is really a measure of the **extent of fragmentation** under a given set of conditions. The fragmentation *begins* at the carbonyl group, and then proceeds further. If there is no carbonyl group in the molecule of a sugar (*e.g.*, sucrose), no fragmentation can occur, and the sugar is therefore *non-reducing.*

The two reagents that are employed to detect the presence of reducing sugars and to estimate them quantitatively are :—

(*i*) **Fehling's reagent,** which contains cupric sulphate, sodium hydroxide and sodium potassium tartrate. The bright blue colour of the solution is due to the presence of a complex tartratocuprate (II) anion.

(*ii*) **Benedict's reagent,** which contains cupric sulphate, sodium carbonate and sodium citrate. The colour of the solution is deep bluish-green due to the presence of a complex citratocuprate (II) anion.

Both the reagents give a bright red precipitate of cuprous oxide with a reducing sugar at the boiling point.

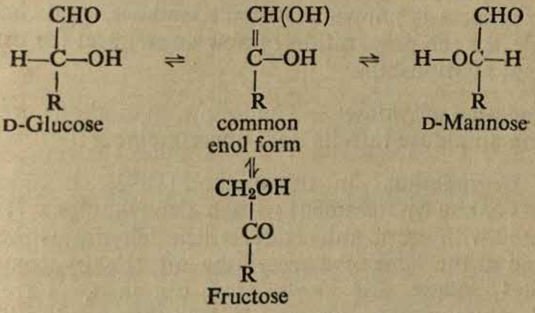
(9) **Reducing Action of Monosaccharides in Acidic Solution.** A characteristic distinctive reaction of monosaccharides is reduction of cupric salts in *acid* solution. Its importance lies in the fact that **disaccharides do not respond** to this test, not even those (*e.g.* lactose) which reduce the alkaline cupric reagents. **Barfoed's reagent,** used for this test, contains cupric acetate and acetic acid. The reagent is boiled in a test-tube, and sugar solution to be tested is added *dropwise*, the liquid being kept boiling all the time. Formation of a faint red scum of cuprous oxide on the surface of the liquid shows the presence of a monosaccharide.

(10) **Furfural-Phenol Reactions.** Concentrated mineral acids convert sugars into derivatives of furfural, which condense with phenols to give highly coloured products.

In **Molisch's test,** which is given by all sugars, 1 drop of alcoholic α-naphthol is added to about 1 ml of the sugar solution to be tested, and the mixed solution is added carefully down the side of the tube into some concentrated sulphuric acid. A violet ring appears at the junction of the two layers.

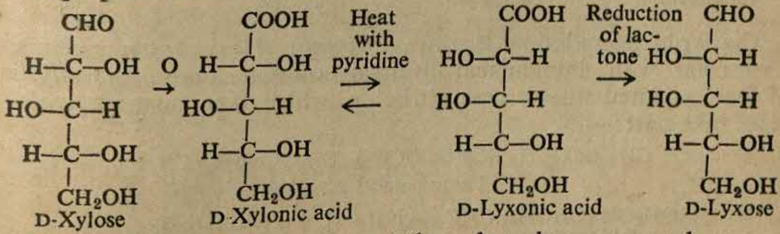
Another important test of this class is **Selivanoff's test given by ketohexoses** (and those disaccharides that give ketohexoses on hydrolysis, *e.g.*, sucrose). The reagent is a solution of resorcinol in hydrochloric acid. The sugar solution to be tested (5 drops) is added to about 2 ml of the reagent, and the liquid boiled for half a minute. A red or brown colour or precipitate is formed. Aldoses do not respond to this test, though in some cases a very faint colour may appear.

7. **Lobry de Bruyn Transformation.**—Sugars that give rise to the same osazone (*e.g.*, D-glucose, D-mannose and D-fructose), differ only in the configuration of No. 2 carbon atom. Any one of them, when treated with **very dilute alkali**, *e.g.*, 0.05N $Ca(OH)_2$, gives an equilibrium mixture of all the three. This reaction, discovered by Lobry de Bruyn and van Ekenstein, probably occurs through the common enol form which can revert to any of the three sugars. Representing the common radical of these sugars by R, we have :—



The reaction has been found of great value in the **synthesis of new sugars.**

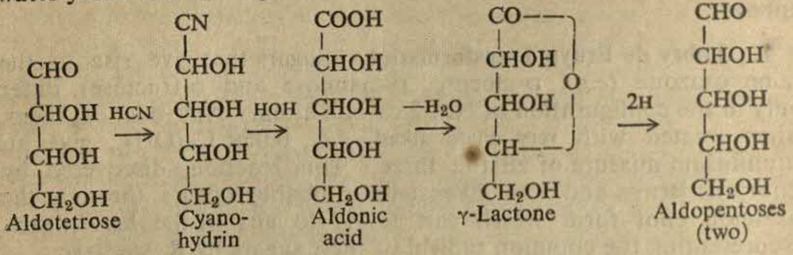
8. **Epimerization of Aldoses.**—An important general method of converting an aldose into its epimer consists in oxidizing the aldose to the monobasic acid and heating the acid with pyridine or quinoline to racemize carbon atom No 2. The mixture of epimeric acids is then separated by suitable methods, and the new acid is converted into its lactone, which, on reduction by sodium amalgam, gives the new aldose. D-Lyxose, for example, which does not occur in nature, was prepared from D-xylose by this method.



In this manner a number of new aldoses have been prepared.

9. **Synthesis of a Higher from a Lower Aldose.**—A tetrose may be converted into pentose and a pentose into a hexose, *etc.*, by a

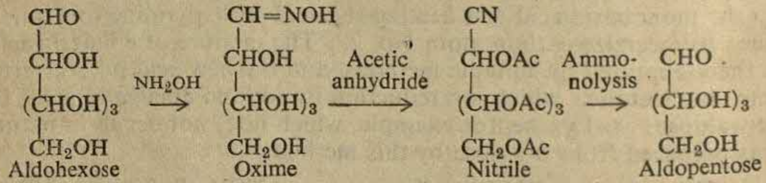
method worked out by Kiliani and Fischer. The aldose is treated with hydrogen cyanide, the resulting cyanohydrin is hydrolysed to the corresponding aldonic acid and the latter converted into its γ-lactone. Reduction of the γ-lactone with sodium amalgam and water yields the two higher aldoses:—



The above process is known as **Kiliani's synthesis,** and has proved very valuable for the preparation of new sugars and for establishing configurational relationships.

10. Degradation of Aldoses.—The following methods are available for converting an aldose into its next lower member:—

(1) **Wohl Degradation.** In this method (1893), the aldose is converted into its oxime by treatment with hydroxylamine. The oxime is then heated with acetic anhydride, which dehydrates the oxime to the nitrile and at the same time acetylates all the hydroxyl groups. The **acetylated aldonic acid nitrile,** thus obtained, is treated with ammoniacal silver nitrate, whereby it loses the acetyl radicals and a molecule of hydrogen cyanide, thus giving an aldose with *one carbon less* than the original sugar. The degradation of analdohexose to the corresponding aldopentose, therefore, involves the following steps:—

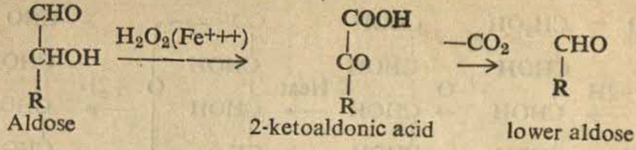


The Wohl degradation is thus a **reversal of cyanohydrin synthesis.** Treatment with ammoniacal silver salt solution causes *ammonolysis* of the acetylated aldonic acid nitrile in which six ammonia molecules take part:—

$$\begin{array}{c}CH_2(OCOCH_3).(CHOCOCH_3)_3.CH(OCOCH_3).CN\\ \downarrow \text{ammoniacal silver salt solution}\\ \underset{\text{Aldopentose}}{CH_2OH.(CHOH)_3.CHO} + NH_4CN + \underset{\text{Acetamide}}{5CH_3CONH_2}\end{array}$$

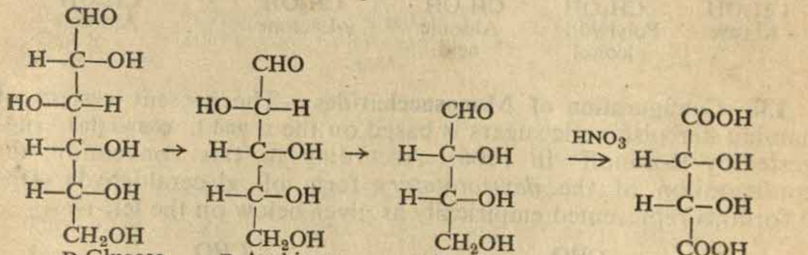
(2) **Ruff Degradation.** Ruff's method (1899) consists in the oxidation of an aldose with hydrogen peroxide in the presence of basic

ferric acetate (catalyst). The α-ketoaldonic acid, first produced, loses carbon dioxide to form the next lower aldose:—



Aldose 2-ketoaldonic acid lower aldose

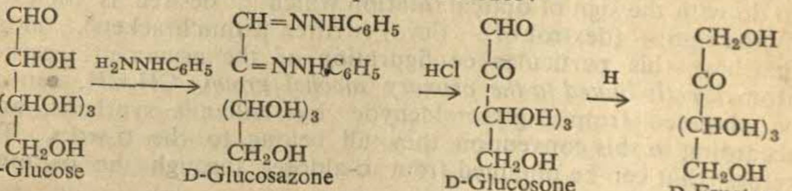
If the configuration of the original aldose is known, the **configurations of degradation products** follows automatically, as shown below for the step-wise degradation of D-glucose:—



D-Glucose D-Arabinose D-Erythrose *meso*-tartaric acid

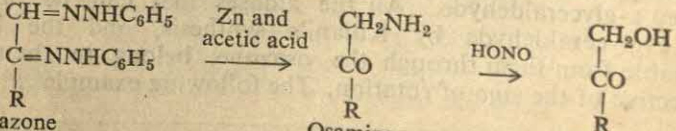
On oxidation with nitric acid, D-erythrose yields *meso*-tartaric acid, which is in full agreement with theory.

11. Conversion of an aldose into a Ketose.—This is carried out through osazone formation. The osazone is hydrolysed with concentrated hydrochloric acid to form an **osone** (a keto-aldehyde), which on reduction with zinc dust and acetic acid gives the ketose (as CHO group is reduced in preference to CO). The conversion of D-glucose into D-fructose takes place as under:—



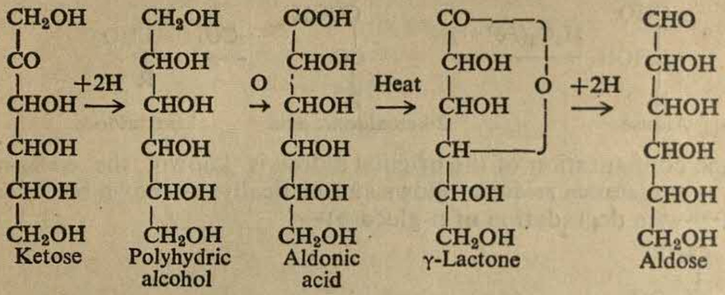
D-Glucose D-Glucosazone D-Glucosone D-Fructose

In another method, the osazone is reduced with zinc and acetic acid to an **osamine** (amino-derivative of a ketose), which on treatment with nitrous acid gives the ketose:—

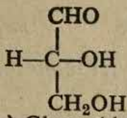


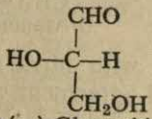
Osazone Osamine Ketose

12. Conversion of a Ketose into an Aldose.—This is carried out by reducing the ketose to the corresponding polyhydric alcohol, which is then oxidised to the aldonic acid. The γ-lactone of this acid on reduction with sodium amalgam in weakly acid solution gives the aldose :—



13. **Configuration of Monosaccharides.**—The present system of naming stereoisomeric sugars is based on the D and L convention suggested by Rosanoff[1] in 1906. According to this convention, the configuration of the *dextrorotatory* form of glyceraldehyde (the D form) is represented empirically as given below on the left :


D(+)-Glyceraldehyde


L(−)-Glyceraldehyde

The CHO group is written uppermost, and the hydroxyl group linked to the asymmetric carbon atom is written (in the case of D form) on the right hand side of the configurational formula. The small capital letter D refers to *configuration only* and has nothing to do with the sign of optical rotation which if desired is indicated by the sign + (dextro) or − (levo) (written within brackets). Aldoses that have this particular configuration of the asymmetric carbon atom *directly linked to the primary alcohol group*, CH_2OH, can all be obtained from D-glyceraldehyde by Kiliani's synthesis, and, according to this convention, they all belong to the D-series. The ketoses that can be obtained from D-aldoses through the osazones also belong to the D-series.

The *levorotatory* form of glyceraldehyde is assigned the alternative configuration, given above (alongside that of the D-form), and is called L-glyceraldehyde. All the aldoses that can be obtained from L-glyceraldehyde by Kiliani's synthesis, and the ketoses obtainable from them through the osazone, belong to the L-series, irrespective of the sign of rotation. The following examples illustrate the system :—

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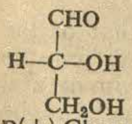
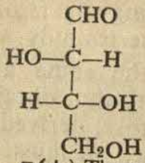
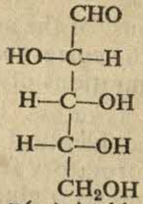
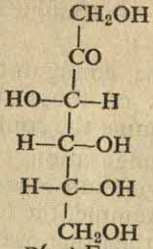
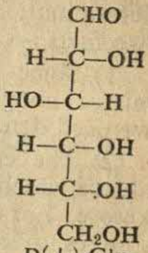
[1] Fischer's suggestion of referring all configurational relationships back to the two optically active forms of glucose led to ambiguities in the gulose-idose series, and has therefore been discarded and replaced by the D and L convention of Rosanoff.

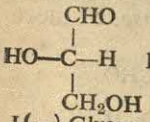

D(+)-Glyceraldehyde

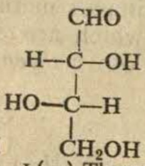

D(+)-Threose

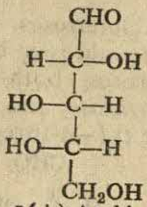

D(−)-Arabinose

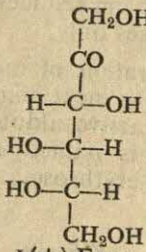

D(−)-Fructose

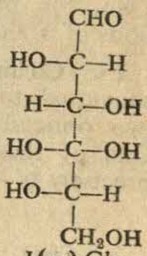

D(+)-Glucose


L(−)-Glyceraldehyde

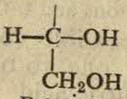

L(−)-Threose


L(+)-Arabinose

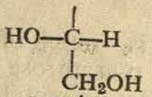

L(+)-Fructose


L(−)-Glucose

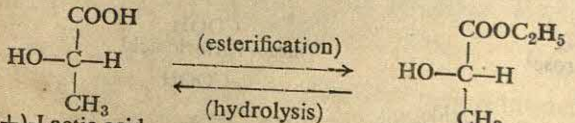
While the series (D or L) to which a sugar belongs is determined by the configuration of the *first asymmetric carbon atom from the bottom of the formula*,


D-series

or


L-series

the observed optical rotation depends on the configuration and the nature of the molecule as a whole. It also depends on the solvent, temperature and the wavelength of the light used. The most important factor, however, that determines the direction of the observed rotation is the *nature of the groups present about the asymmetric carbon atom*. Thus, L(+)-lactic acid, on esterification, gives L(−)-ethyl lactate :—



L(+)-Lactic acid
L(−)-Ethyl lactate

The esterification (or the reversal of it) could not change the *configuration* of the molecule, though it has changed the observed rotation, *i.e.*, the *dextro*-rotatory lactic acid has given a *levo*-rotatory ester. The D and L convention serves to keep track of the **configurational relationship** of molecules. The sign of rotation, *d*- or *l*-, would be altogether useless for this purpose.

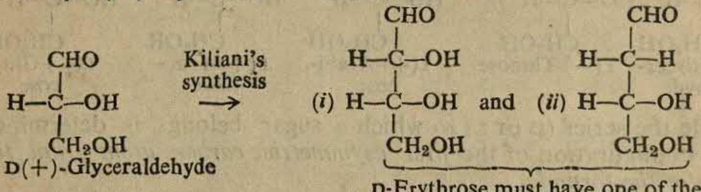
14. Determination of Configuration of Monosaccharides.—The determination of configuration of monosaccharides is simplified by two facts :—

(1) Since the configurations of the sugars of the L-series are the mirror images of those of the corresponding sugars of the D-series, we need determine the configurations of D-series only.

(2) The configuration of a ketose is the same as that of the aldose which gives an osazone, identical with that obtained from the ketose. For example, the levorotatory fructose, derived from natural sources, gives the same osazone as D-glucose. It must, therefore, be designated as D-fructose.

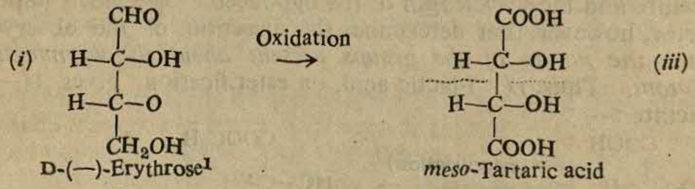
So, the problem reduces itself to the determination of configurations of D-aldoses only.

15. Configuration of D-Aldotetroses.—When D-glyceraldehyde is converted to the next higher aldoses by Kiliani's method, we get two optically active aldotetroses, both of which are *levorotatory*. One of these is named *erythrose* and the other *threose*, or more precisely D(—)-erythrose and D (—)-threose.

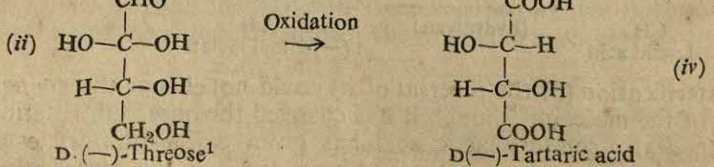


D-Erythrose must have one of these configurations and D-threose the other.

The problem is, which of these two possible configurations must be assigned to D-erythrose and which one to D-threose ? When submitted to oxidation with hot, dilute nitric acid, D-erythrose yields optically inactive *meso*-tartaric acid, while D-threose gives optically *active* tartaric acid (levorotatory). These facts lead to the following configurations :—



D-(—)-Erythrose[1] *meso*-Tartaric acid



D-(—)-Threose[1] D(—)-Tartaric acid

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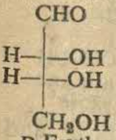
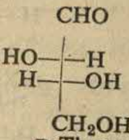
[1] The designation *erythro* signifies that in the projection formula the two OH groups have a *cis* relationship. The prefix *threo* signifies *trans* relationship of the CH groups.

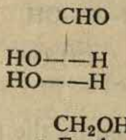
The *meso*-tartaric acid, being inactive and non-resolvable, must be assigned configuration (*iii*) which has a plane of symmetry (indicated by the dotted line, the lower half of the formula being the mirror image of the upper half). The rest of the argument is self-evident.

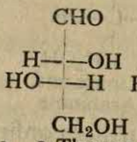
The same conclusion could have been arrived at equally well by reducing the erythrose and threose to the corresponding alcohols (tetritols). The former gives the optically inactive, non-resolvable erythritol (meso) and the latter the optically active D-threitol (which is dextrorotatory in water and levorotatory in alcohol).

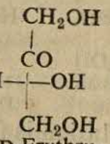
16. Configuration of all the six Tetroses.—We are now in a position to write the configurations of all the six tetroses theoretically possible (all of which are known). Four of these are aldoses and two ketoses (D-erythrulose and L-erythrulose). We shall here use the **simplified projection formulæ** in which the asymmetric carbon atoms are omitted :—

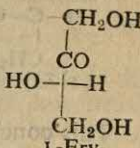

D-Erythrose


D-Threose


L-Erythrose


L Threose


D-Erythrulose


L-Erythrulose

17. Simpler Representation of Configuration.—A very simple method of representing configurations of sugars consists in the use of signs + and −, the former indicating the H—C—OH (hydroxyl-to-right) configuration of an asymmetric carbon atom in the projection formulae given above and the latter the HO—C—H (hydroxyl-to-left) configuration. We may re-write the configurations of the six tetroses to illustrate the system :—

D-Erythrose	D-Threose	L-Erythrose	L-Threose	D-Erythrulose	L-Erythrulose
+	−	−	+		
+	+	−	−	+	−

Another method consists in turning each arrangement *clockwise* through an angle of 90°, when we get the simplest configurational representation of sugars used in the literature of organic chemistry. The above six configurations then become :—

+ + + − − − − + + −

18. Configuration of Aldopentoses.—According to theory, 8 (*i.e.* 2^3) aldopentoses are possible, four belonging to the D-series and the other four to the L-series. Their configurations must be :—

D Series	+ + +	+ + −	+ − +	+ − −
L Series	− − −	− − +	− + −	− + +

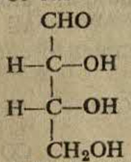
The configurations of the L-series sugars, of course, are the mirror images of those of the D-series. Hence, if we determine the configurations of the four D-aldopentoses, those of the other four can be readily deduced.

All the **eight aldopentoses** are known. Two of these, namely D-ribose and D-arabinose, are related to the tetrose D-erythrose and two others, namely D-xylose and D-lyxose, are similarly related to D-threose, as shown below :—

$$\text{D-Erythrose} \;\underset{\text{Degradation}}{\overset{\text{Kiliani's synthesis}}{\rightleftarrows}}\; \left\{\begin{array}{l}\text{D-Ribose}\\ \text{D-Arabinose}\end{array}\right.$$

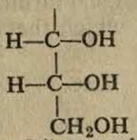
$$\text{D-Threose} \;\underset{\text{Degradation}}{\overset{\text{Kiliani's synthesis}}{\rightleftarrows}}\; \left\{\begin{array}{l}\text{D-Xylose}\\ \text{D-Lyxose}\end{array}\right.$$

This relationship gives the configurations of the *two* asymmetric carbon atoms nearest to the CH_2OH group of the four aldopentoses, (*i.e.*, of carbon atoms 3 and 4), as shown below :—



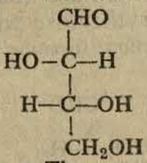
$$\begin{array}{c}\text{CHO}\\ |\\ \text{H—C—OH}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Erythrose



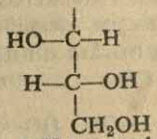
$$\begin{array}{c}|\\ \text{H—C—OH}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Ribose and D-Arabinose



$$\begin{array}{c}\text{CHO}\\ |\\ \text{HO—C—H}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Threose

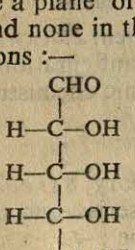


$$\begin{array}{c}|\\ \text{HO—C—H}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Xylose and D-Lyxose

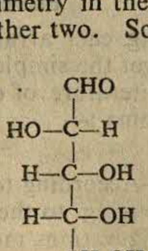
This conclusion is further confirmed by the fact that D-ribose and D-arabinose give the same osazone, and are therefore *epimeric* with each other (*i.e.*, they differ *only* in the configuration of the *alpha*-carbon). Similarly, D-xylose and D-lyxose are epimeric with each other, as they give the same osazone (different from that of D-ribose and D-arabinose).

To determine the configuration of the remaining asymmetric carbon atom, we submit the above four aldopentoses to oxidation with nitric acid[1]. D-Ribose and D-xylose give dibasic acids that are optically inactive and non-resolvable, *i.e.*, *meso*-trihydroxyglutaric acids (named *ribo-* and *xylo-* trihydroxyglutaric acids respectively). The other two sugars give optically active acids. Hence, there must be a plane of symmetry in the molecules of D-ribose and D-xylose and none in the other two. So, we have the four required configurations :—



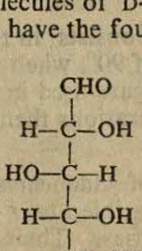
$$\begin{array}{c}\text{CHO}\\ |\\ \text{H—C—OH}\\ |\\ \text{H—C—OH}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Ribose



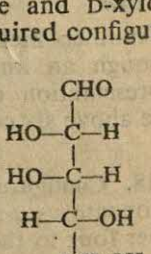
$$\begin{array}{c}\text{CHO}\\ |\\ \text{HO—C—H}\\ |\\ \text{H—C—OH}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Arabinose



$$\begin{array}{c}\text{CHO}\\ |\\ \text{H—C—OH}\\ |\\ \text{HO—C—H}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Xylose



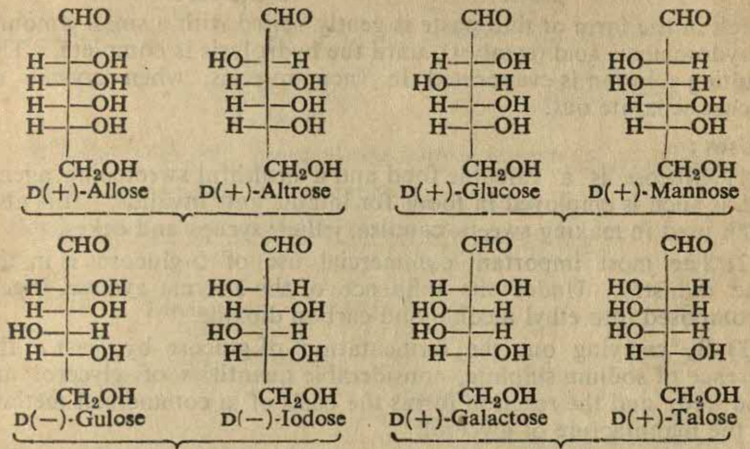
$$\begin{array}{c}\text{CHO}\\ |\\ \text{HO—C—H}\\ |\\ \text{HO—C—H}\\ |\\ \text{H—C—OH}\\ |\\ CH_2OH\end{array}$$

D-Lyxose

19. Aldohexoses.—All the sixteen aldohexoses are known. The configuration, name and sign of optical rotation of each of the eight aldohexoses of the D-series are tabulated below. Each pair of epimeric sugars is enclosed within a bracket.

---

[1] The same results are arrived at by reducing the four D-aldopentoses to the corresponding meso and optically active pentan-pentols (or 'pentitols').



20. D-Glucose (*Grape-sugar*, *Dextrose*, *Corn-sugar*) :—

Occurrence. In the free state, this sugar occurs in sweet fruits, particularly grapes (hence the name *Grape-sugar*). Small, but nearly constant, amount of glucose is present in the animal blood Large quantities of glucose are present in the urine of people suffering from *diabetes mellitus*.

Most of the di- and polysaccharide molecules are built up of D-glucose units. Maltose, starch and cellulose are built up entirely of D-glucose, while cane-sugar and milk-sugar are composed of D-glucose and another monosaccharide (D-fructose in the former and D-galactose in the latter). Thus, D-glucose is the chief product of digestion of carbohydrate food in our bodies, and serves as the major source of energy and body heat.

D-Glucose also enters into the composition of natural *glucosides* (*e.g.*, *amygdalin* of bitter almonds and *salicin* of willow-bark) and of many *tannins*. The latter, on hydrolysis, give D-glucose along with tannic acid.

Laboratory Preparation. D-Glucose can be readily obtained in the laboratory by heating cane-sugar (sucrose) with alcohol and a little concentrated hydrochloric acid. The cane-sugar is thus hydrolysed into D-glucose and D-fructose :

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{D-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-Fructose}}{C_6H_{12}O_6}$$

On allowing the reaction mixture to cool, glucose, being much less soluble in alcohol than fructose, crystallizes out.

Manufacture. D-Glucose is prepared on the commercial scale by the hydrolysis of starch (corn-starch in U.S.A. and potato-starch in Europe) :—

$$\underset{\text{Starch}}{(C_6H_{10}O_5)x} + xH_2O \rightarrow \underset{\text{D-Glucose}}{xC_6H_{12}O_6}$$

Starch in the form of thin paste is gently boiled with a small amount of hydrochloric acid (catalyst), until the hydrolysis is complete. The resulting solution is evaporated in vacuum pans, when crystals of glucose separate out.

Uses :—

(1) Glucose is a valuable food and a healthful sweetening agent, and as such is employed in foods for infants and invalids. It is also much used in making sweets, candies, jellies, syrups and cakes.

(2) The most important commercial use of D-glucose is in the wine industry. Under the influence of the enzyme *zymase*, it gets decomposed into ethyl alcohol and carbon dioxide.

(3) By carrying out the fermentation of glucose by yeast in the presence of sodium sulphite, considerable quantities of glycerol are produced, and the reaction forms the basis of a commercial method for the manufacture of glycerol.

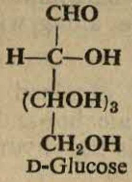
(4) D-Glucose is the starting material for the synthetic manufacture of vitamin C.

(5) A minor use of glucose is as a reducing agent in the silvering of mirrors and in vat-dyeing with indigo.

(6) A pure solution of D-glucose is given intravenously in conditions which lower the natural glucose content in blood.

Physical Properties. D-Glucose is a colourless, crystalline substance, much less sweet than cane-sugar. It is readily soluble in water, from which it separates as crystals containing 1 molecule of water and melting at 80°. It is sparingly soluble in alcohol, from which it crystallizes as anhydrous needles, melting 146°. It is dextrorotatory, and shows *mutarotation*.

Chemical Reactions. D-Glucose shows all the characteristic reactions of an *aldose* that have already been described in detail in earlier sections. We give below a complete summary of these reactions :—



$$\begin{array}{c} CHO \\ | \\ H{-}C{-}OH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

D-Glucose

$$(1)\ \xrightarrow{\text{Acetic anhydride}} \underset{\text{D-Glucose pentaacetate}}{CH_2OAc(CHOAc)_4CHO}$$

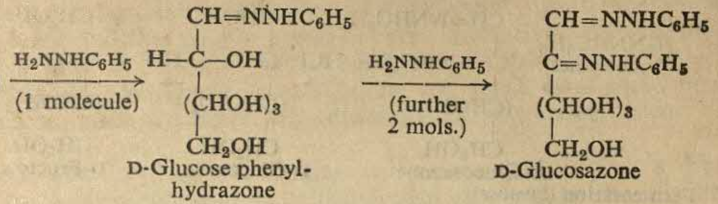
$$(2)\ \xrightarrow{\text{Reduction (Na-Hg)}} \underset{\text{D-Sorbitol}}{CH_2OH(CHOH)_4CH_2OH}$$

$$(3)\ \xrightarrow{\quad HCN \quad} \underset{\text{D-Glucose cyanohydrin}}{CH_2OH(CHOH)_4CH(OH)CN}$$

$$(4)\ \xrightarrow{\text{Oxidation } (Br_2+H_2O)} \underset{\text{D-Gluconic acid}}{CH_2OH(CHOH)_4COOH}$$

$$(5)\ \xrightarrow{\text{Oxidation with } HNO_3} \underset{\text{D-Glucosaccharic acid}}{HOOC(CHOH)_4COOH}$$

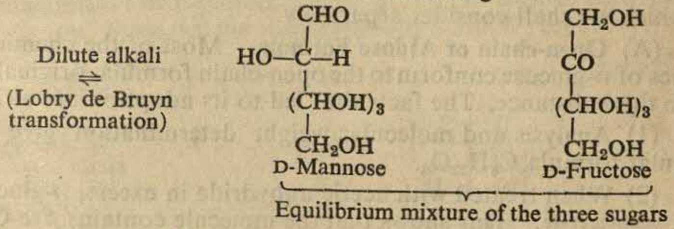
$$(6)\ \xrightarrow{\quad NH_2OH \quad} \underset{\text{D-Glucose oxime}}{CH_2OH(CHOH)_4CH{=}NOH}$$

(7) 

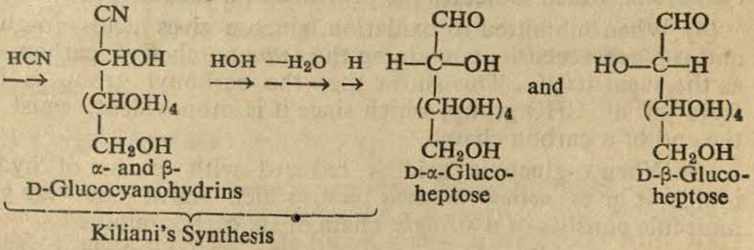
(8) Reduces Fehling's, Benedict's and Barfoed reagents →Cu_2O (red ppt.)

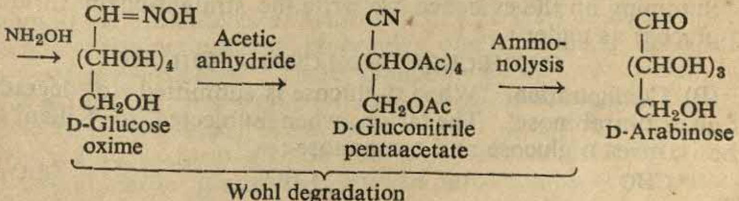
(9) Reduces ammoniacal silver nitrate →silver mirror

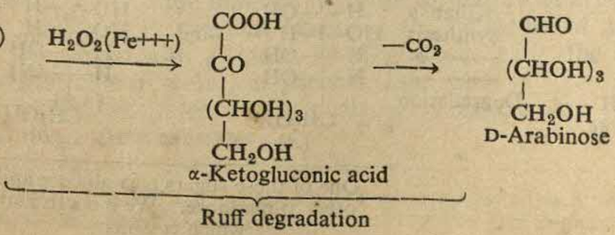
(10) α-naphthol and conc. H_2SO_4(Molisch's test →violet ring

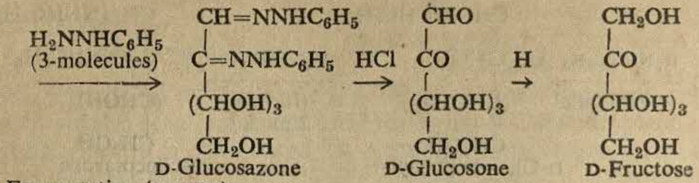
(11) 

(12) $\underbrace{\xrightarrow[\text{tion}]{\text{Oxida-}} \text{D-Gluconic acid} \xrightarrow[\text{pyridine}]{\text{Heat with}} \text{D-Mannonic acid}}_{\text{Epimerization}} \xrightarrow[\text{lactone}]{\text{Reduce the}} \text{D-Mannose}$

(13) 

(14) 

(15) 

(16) 

$$\xrightarrow[\text{(3-molecules)}]{H_2NNHC_6H_5} \underset{\text{D-Glucosazone}}{\begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} \xrightarrow{HCl} \underset{\text{D-Glucosone}}{\begin{array}{l} CHO \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} \xrightarrow{H} \underset{\text{D-Fructose}}{\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}}$$

(17) $\xrightarrow{\text{Fermentation } (zymose)}$ $\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$

(18) $\xrightarrow{CH_3OH(HCl)}$ α- and β-methyl-D-glucosides (see sec. 21, p. 506).

21. Constitution of D-Glucose.—There are three different aspects of the problem of the determination of constitution of D-glucose, which we shall consider separately.

(A) **Open-chain or Aldose Formula.** Most of the chemical properties of D-glucose conform to the open-chain formula, originally assigned to this substance. The facts that led to its adoption are as follows:—

(1) Analysis and molecular weight determination give the molecular formula $C_6H_{12}O_6$.

(2) When treated with acetic anhydride in excess, D-glucose forms a **pentaacetate.** This shows that the molecule contains *five* OH groups. Since D-glucose is a stable compound that does not lose water easily, the five OH groups must each be linked to a *different* carbon atom.

(3) D-Glucose adds one molecule of hydrogen cyanide to form a **cyanohydrin**, which indicates the presence of a carbonyl group.

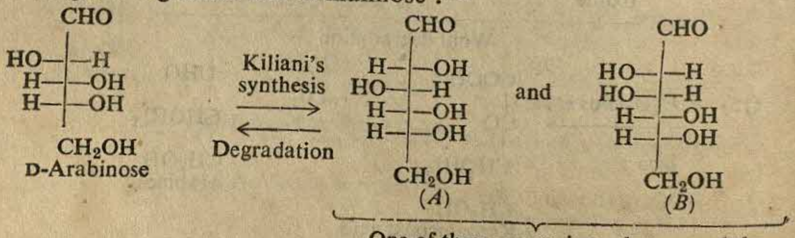
(4) When submitted to oxidation, glucose gives acids (D-gluconic and D-glucosaccharic) containing the *same* number of carbon atoms as the sugar itself. This shows that the carbonyl group is in the form of a—CHO group, which since it is monovalent, must be at the end of a carbon chain.

(5) When D-gluconic acid is reduced with excess of hydrogen iodide, it gives **normal hexanoic acid**, which shows that the glucose molecule consists of a *straight* chain of six carbon atoms.

Summing up the evidence, we write the straight-chain formula of D-glucose as under :—

$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO$$

(B) **Configuration.** When D-glucose is submitted to degradation, it gives D-arabinose. The latter, when subjected to Kiliani's synthesis, gives D-glucose and D-mannose :—

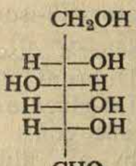


One of these sugars is D-glucose and the other D-mannose. We have to find out which is which.

These facts show that D-glucose and D-mannose are epimeric[1] with each other and that they possess, between themselves, the configurations *A* and *B* (which follow from that of D-arabinose, already established). We have to assign one of these configurations to D-glucose, when the other will automatically go to D-mannose.

Now, when D-glucose is oxidized with nitric acid, it gives a dibasic acid (D-glucosaccharic acid), which is also obtained by the oxidation of another aldohexose, namely L-gulose.

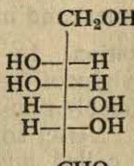
Hence, it follows that if the terminal groups —CHO and —CH_2OH in the D-glucose configuration be interchanged, we would get the configuration of D-gulose. If we do this in each of the configurations *A* and *B*, we get the configurations *C* and *D* respectively :—



$$\begin{array}{rcl} & CH_2OH & \\ H- & | & -OH \\ HO- & | & -H \\ H- & | & -OH \\ H- & | & -OH \\ & CHO & \end{array}$$

(*C*)

and



$$\begin{array}{rcl} & CH_2OH & \\ HO- & | & -H \\ HO- & | & -H \\ H- & | & -OH \\ H- & | & -OH \\ & CHO & \end{array}$$

(*D*)

By rotating the configurations *C* and *D* in the plane of the paper through 180°, we see that it is the configuration *C* which is different from A, and that *D* is identical with B. Hence we conclude that the configuration *C* belongs to L-gulose, *A* to D-glucose and *B* to D-mannose.

(C) **Cyclic Structure : —**

(1) **Existence of two methylglucosides.** A new aspect of the constitution of glucose presented itself by the discovery of two **methylglucosides** by Emil Fischer in 1894. He found that glucose reacts with methyl alcohol in the presence of anhydrous HCl (catalyst) to give a mixture of two stereoisomeric methyl glucosides, one of which is dextro- and the other levo-rotatory. These compounds *do not react with hydrogen cyanide, hydroxylamine, or phenylhydrazine, and, therefore, contain no CHO group.* When heated with dilute acids, they are hydrolysed to re-form glucose and methyl alcohol. It is thus clear that the aldehyde group has entered into combination with the alcohol in the same manner as in the formation of acetals (page 273). But, since in the present case only *one* molecule of methyl alcohol has combined with a molecule of glucose, with the elimination of one molecule of water, it follows that one of the alcohol groups of the glucose molecule must also have taken part in the process, forming a **cyclic anhydride :**

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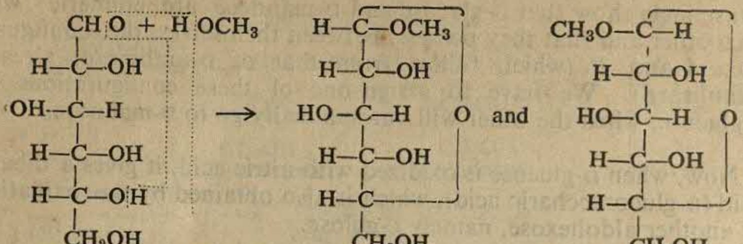
[1] That D-glucose and D-mannose are epimeric with each other also follows from the fact that they both give the *same* osazone (*viz.* D-glucosazone).



D-Glucose Methyl alcohol α-Methyl-D-glucoside (*dextro-*) β-Methyl-D-glucoside (*levo-*)

The moment the ring comes into existence, the aldehydic carbon atom becomes asymmetric, and hence we get *two* stereoisomers. In one of these, the newly produced asymmetric carbon atom is dextrorotatory (α-isomer) and in the other it is levorotatory (β-isomer).

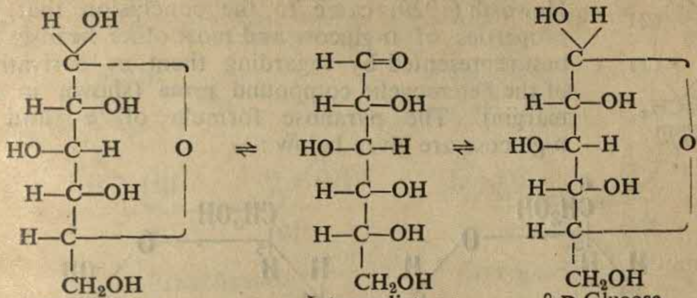
(2) **Mutarotation.** In 1846, long before Fischer's discovery of α- and β-methylglucosides, it was discovered by Dubrunfaut that the rotation of a freshly prepared aqueous solution of D-glucose decreased rather rapidly. After some time, the value became constant. This phenomenon, called *mutarotation*, is shown by all aldoses and ketoses.

(3) **Isolation of α- and β- forms of D-Glucose.** The existence of α- and β-methylglycosides on the one hand and the phenomenon of mutarotation shown by D-Glucose on the other, led Tarnet (1895) to the actual separation of the α- and β- forms of D-glucose itself. When a concentrated aqueous solution of D-glucose is evaporated at 30° to 35°, α-D-glucose separates out. It melts at 146°, and has a specific rotation of +109·6°. β-D-Glucose is best prepared by crystallizing D-glucose from hot pyridine. It melts at 148° to 150°, and its specific rotation is +20·5°. Both forms show mutarotation :—

$$\underset{\substack{\text{(sp. rotation}\\ \text{109·6°)}}}{\text{α-D-Glucose}} \rightleftharpoons \underset{\substack{\text{(consisting of 37\% α-}\\ \text{and 63\% β-) with}\\ \text{specific rotation 52·7°}}}{\text{Equilibrium mixture}} \rightleftharpoons \underset{\substack{\text{(sp. rotation,}\\ \text{+20·5°)}}}{\text{β-D-Glucose}}$$

(4) **Analogy between α- and β-Glucose and α- and β-Methylglucosides.** This was conclusively established by E. F. Armstrong in 1903. It was already known from Fischer's work that certain enzymes have the specific ability to hydrolyse α- or β-glucosides but not both. For example, *maltase* (from yeast) hydrolyses only the α-, while *emulsin* (from bitter almonds) hydrolyses only the β-forms. Armstrong followed the enzymatic hydrolysis in a polarimeter, and demonstrated that the glucose set free from the α-glucoside had a high rotation and was therefore α-D-glucose. On the other hand, the glucose from the β-glucoside had a very low rotation, and was therefore α-D-glucose.

α- and β- forms of D-glucose are consequently given the **cyclic structures** similar to those of the corresponding α- and β- forms of methylglucosides. The mutarotation is considered as being due to the change of α- into the β-form, and *vice versa*, through the open-chain aldehydic form :—

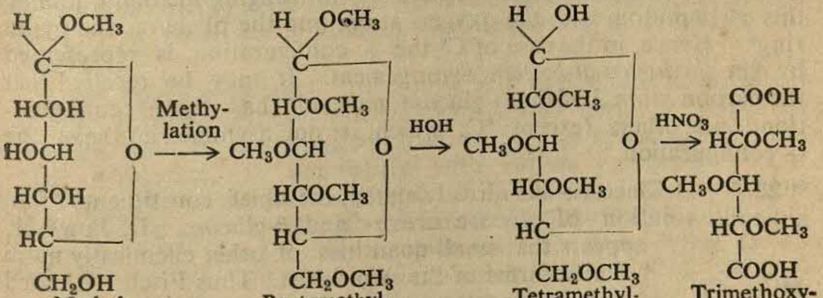


α-D-Glucose ⇌ Intermediate aldehydic form[1] ⇌ β-D-Glucose

It may be noted that the α- and β- forms of D-glucose are *not* optical antipodes, as the only difference in their configurations lies in the space arrangement of the newly produced asymmetric carbon atom. Hence, they possess different physical properties, and are therefore separable by their different solubilities in various solvents.

Another point that should be noted is that the relative positions of the two hydroxyl groups on C_1 and C_2 in the case of α-D-glucose is *cis*, and in the β-form it is *trans*.

(5) **Size of D-Glucose Ring.** That the D-glucose ring is 6-membered (and not 5-membered as originally supposed) was conclusively established by W.N. Haworth (1926). He submitted α-methyl-D-glucoside[2] to a three-step process consisting of: (*i*) methylation, (*ii*) hydrolysis, and (*iii*) destructive oxidation of the product. The final product obtained was a **trimethoxyglutaric acid**, showing the presence of a six-membered ring :—

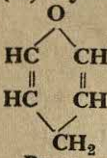


α-Methyl-D-glucoside → Pentamethyl-D-glucose → Tetramethyl-D-glucose → Trimethoxy-glutaric acid

---

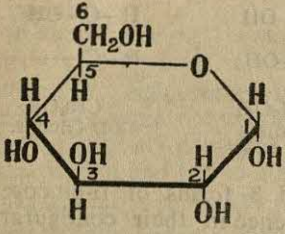
[1] According to Lowry (1925) the conversion α-form ⇌ β-form involves the addition of a molecule of water at the aldehyde group to form an **aldehydrol** which then loses a molecule of water between one of the two newly introduced hydroxyl groups and the hydroxyl group in the δ-position.

[2] β-isomer serves equally well.

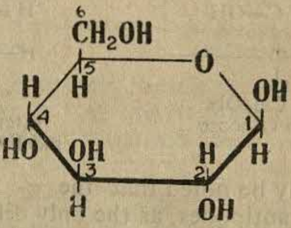


Pyran

(*vi*) **Pyranose Formula of D-Glucose.** As the result of extensive researchwork on sugars and their derivatives, Haworth (1929) came to the conclusion that the properties of D-glucose and most other hexoses are best represented by regarding them as derivatives of the heterocyclic compound **pyran** (shown in the margin). The pyranose formula of α- and β-D-glucose are given below :—



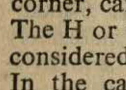
α-D-Glucopyranose



β-D-Glucopyranose

In writing the pyranose formula, it may be remembered that the pyran ring is in the plane of the paper, and that to make the plane better visualized it is shaded in the "front" by use of bold lines. Starting with the oxygen atom (placed at the upper right corner of the ring) and proceeding *clockwise*, are placed at each successive corner, carbon atoms[1] 1, 2, 3, 4 and 5, all of which are asymmetric. The H or OH joined to carbon atoms by lines extending *upwards* are considered as lying *above* the plane of the pyran ring, and *vice versa*. In the case of all asymmetric carbon atoms except the last one (*i.e.* C^5) the + configuration is represented by the **hydroxyl-at-bottom arrangement** and the — configuration by the hydrogen-at-bottom arrangement. In the case of C^5, however, there is an *apparent* displacement of the groups which arises out of the necessity of bringing the bond, joining this carbon atom with the oxygen atom, into the plane of the pyran ring[2]. Hence, in the case of C^5 the + configuration is represented by the *hydrogen-at-bottom* arrangement. It may be recalled that the carbon atom 3 of the D-glucose molecule has the — configuration ; all others (except ^6C, which is not asymmetric) have the + configuration.

22. γ-D-Glucose.—As already stated, the chief constituents of an aqueous solution of glucose are α- and β-glucose. It, however, appears that small quantities of other chemically more reactive forms of the sugar exist. Thus Fischer isolated two isomeric tetramethyl derivatives of what is known as γ-*glucose*. The sugar itself has not been isolated so far, as it is very much less stable and more easily



Furan

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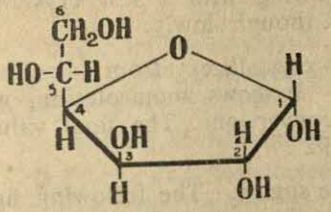
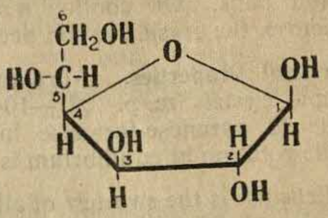
[1] In writing these formulae, the carbon atoms are generally omitted; they are assumed to be at each corner except at the one where the oxygen atom is.

[2] That the displacement is apparent and not real may be readily seen by converting the open-chain aldehydic model into the cyclic form.

oxidizable than the two forms already described. Haworth has assigned the furanose[1] structure to the α- and β- forms of γ-glucose:



α-D-Glucofuranose



β-D-Glucofuranose

KETOHEXOSES

23. **D-Fructose,** *Fruit-sugar*, *Levulose*.—Of the eight possible stereoisomeric ketohexoses, D-fructose is the best known. Its abundant presence in sweet fruits has given it the name "*fruit sugar*". Its solutions rotate polarized light to the left ; hence the name *levulose*. But, as the **asymmetric carbon atom in direct union with the CH_2OH group has the D-configuration** (*i.e.*, hydroxyl-to-right arrangement), the sugar belongs to the D-series and the name D-fructose, therefore, is the most appropriate one.

Occurrence. D-Fructose occurs in the free state, along with D-glucose, in sweet fruits and honey. The great sweetness of honey, which is essentially a supersaturated solution of D-fructose and D-glucose, is due to the preponderance of the former. When honey granulates, it is the D-glucose that crystallizes out.

D-Fructose is one of the two components of the disaccharide D-Sucrose, the other one being D-glucose. The polysaccharide *inulin* that occurs in the tubers of the Jerusalem artichoke (wild sunflower), dahlia and chicory gives D-fructose as the sole product of hydrolysis. It is from these latter sources that D-fructose is prepared commercially.

Laboratory Preparation. D-fructose may be obtained in the laboratory from cane-sugar by hydrolysis with dilute sulphuric acid. The reaction product, consisting of an equimolecular mixture of D-glucose and D-fructose, is neutralized with barium carbonate and the resulting barium sulphate is filtered off. The filtrate is concentrated, cooled in ice and treated with the calculated quantity of lime, when the sparingly soluble **calcium fructosate** separates, while glucose remains in solution. The calcium compound is filtered, suspended in water and decomposed with carbon dioxide. The precipitated calcium carbonate is filtered off, and the filtrate concentrated to recover fructose.

Commercial Preparation. As already stated, D-fructose is prepared commercially from the polysaccharide *inulin*. This is hydrolysed by boiling with dilute sulphuric acid. The resulting solution containing D-fructose is neutralized with barium hydroxide The barium sulphate is filtered off, and the filtrate is concentrated in vacuum pans. On cooling and sowing with a few crystals of D-fructose, the crystallization occurs, though slowly.

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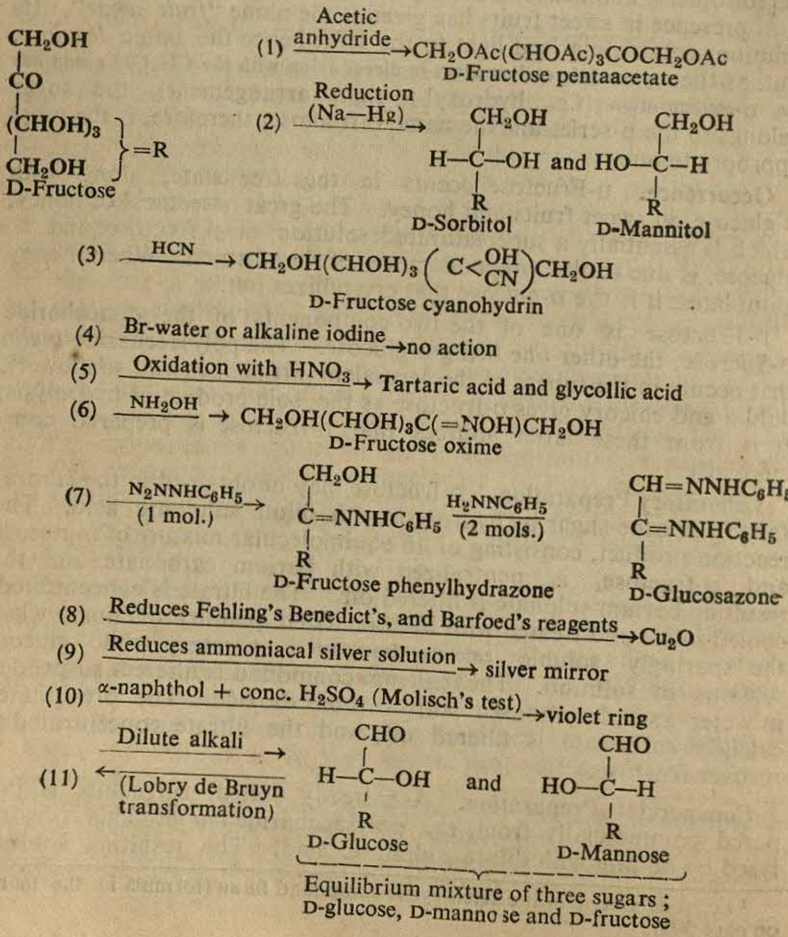
[1] *i.e.*, a derivative of the **heterocyclic compound furan** (formula in the margin on page 508).

Physcial Properties. D-Fructose crystallizes from alcohol as rhombic crystals (m. p. 102°—104°). It shows mutarotation, which is due to pyranose-furanose interconversion. The final value of specific rotation at equilibrium is —92°.

D-Fructose is the sweetest of all the sugars. The following figures show the relative sweetness of various sugars that we use as food :—

Cane Sugar=100 Milk Sugar=16 D-Glucose=73 D-Fructose=173

Reactions. The reactions of D-fructose are those of a typical *ketose* that have all been described in earlier sections. Here is a complete summary :—



$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \Big\} = R$$

D-Fructose

(1) $\xrightarrow{\text{Acetic anhydride}} CH_2OAc(CHOAc)_3COCH_2OAc$

D-Fructose pentaacetate

(2) $\xrightarrow[\text{(Na—Hg)}]{\text{Reduction}} \begin{array}{c} CH_2OH \\ | \\ H-C-OH \\ | \\ R \end{array}$ and $\begin{array}{c} CH_2OH \\ | \\ HO-C-H \\ | \\ R \end{array}$

D-Sorbitol D-Mannitol

(3) $\xrightarrow{HCN} CH_2OH(CHOH)_3\left(C<^{OH}_{CN}\right)CH_2OH$

D-Fructose cyanohydrin

(4) $\xrightarrow{\text{Br-water or alkaline iodine}}$ no action

(5) $\xrightarrow{\text{Oxidation with } HNO_3}$ Tartaric acid and glycollic acid

(6) $\xrightarrow{NH_2OH} CH_2OH(CHOH)_3C(=NOH)CH_2OH$

D-Fructose oxime

(7) $\xrightarrow[\text{(1 mol.)}]{N_2NNHC_6H_5} \begin{array}{l} CH_2OH \\ | \\ C=NNHC_6H_5 \\ | \\ R \end{array} \xrightarrow[\text{(2 mols.)}]{H_2NNC_6H_5} \begin{array}{l} CH=NNHC_6H_5 \\ | \\ C=NNHC_6H_5 \\ | \\ R \end{array}$

D-Fructose phenylhydrazone D-Glucosazone

(8) $\xrightarrow{\text{Reduces Fehling's Benedict's, and Barfoed's reagents}} Cu_2O$

(9) $\xrightarrow{\text{Reduces ammoniacal silver solution}}$ silver mirror

(10) $\xrightarrow{\alpha\text{-naphthol + conc. } H_2SO_4 \text{ (Molisch's test)}}$ violet ring

(11) $\underset{\text{(Lobry de Bruyn transformation)}}{\overset{\text{Dilute alkali}}{\rightleftarrows}} \begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ R \end{array}$ and $\begin{array}{c} CHO \\ | \\ HO-C-H \\ | \\ R \end{array}$

D-Glucose D-Mannose

Equilibrium mixture of three sugars ; D-glucose, D-mannose and D-fructose

(12) $\xrightarrow{Ca(OH)_2}$ sparingly soluble calcium D-fructosate

(13) $\xrightarrow{\text{Fermentation (Zymase)}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$

Uses. The chief use of D-fructose is as food, especially in the form of honey.[1] It is a convenient sweetening agent in the diet of persons suffering from diabetes.

24. Constitution of D-Fructose.

(A) Open-chain or ketose formula :—

(1) Analysis and molecular weight determination give the molecular formula $C_6H_{12}O_6$.

(2) With acetic anhydride, D-fructose gives a pentaacetate. Hence, the molecule contains five OH groups. These must be linked to five *different* carbon atoms, as fructose is a stable compound that does not lose water easily.

(3) D-Fructose reacts with hydrogen cyanide, hydroxylamine and phenylhydrazine. So the molecule must contain a carbonyl group also.

(4) Since D-fructose gives the same osazone as D-glucose, and since D-glucose has been shown to possess a straight chain of six carbon atoms, D-fructose molecule must also consist of a *straight* chain of six carbon atoms.

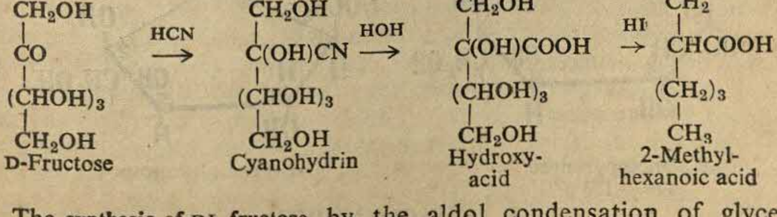
(5) When submitted to oxidation, with nitric acid, it gives a mixture of tartaric acid and glycollic acid. The former being a 4-carbon and the latter a 2-carbon acid, D-fructose must be a ketose with the —CO— group at position 2 of the chain.

Hence, we conclude that the D-fructose molecule must be represented by the formula

$$\overset{6}{C}H_2OH.\overset{5}{C}HOH.\overset{4}{C}HOH.\overset{3}{C}HOH.\overset{2}{C}O.\overset{1}{C}H_2OH$$

The cleavage that occurs on oxidation is obviously between C-2 and C-3.

That D-fructose is a straight-chain ketohexose with the CO group at position 2 of the chain was originally deduced by Kiliani from the following series of reactions leading to the production of **2-methylhexanoic acid :—**



$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \text{D-Fructose} \end{array} \xrightarrow{HCN} \begin{array}{c} CH_2OH \\ | \\ C(OH)CN \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \text{Cyanohydrin} \end{array} \xrightarrow{HOH} \begin{array}{c} CH_2OH \\ | \\ C(OH)COOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \text{Hydroxy-} \\ \text{acid} \end{array} \xrightarrow{HI} \begin{array}{c} CH_2 \\ | \\ CHCOOH \\ | \\ (CH_2)_3 \\ | \\ CH_3 \\ \text{2-Methyl-} \\ \text{hexanoic acid} \end{array}$$

The **synthesis of** DL-**fructose** by the aldol condensation of glyceraldehyde and dihydroxyacetone in the presence of dilute alkali is in full accord with the above constitution of fructose :—

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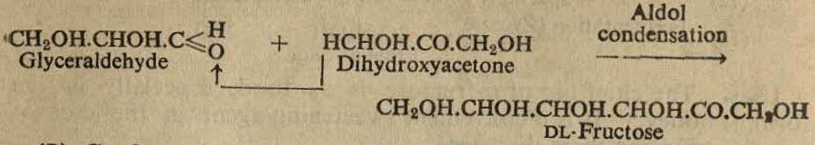
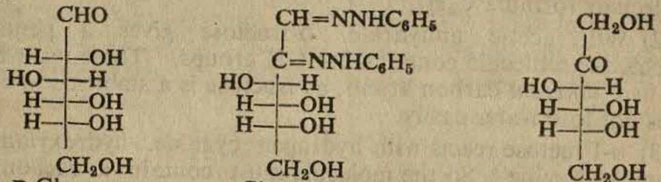
[1] See footnote at page 518.



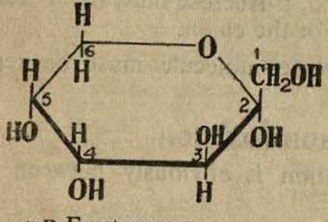
$$\underset{\text{Glyceraldehyde}}{CH_2OH.CHOH.C{<}^{H}_{O}} + \underset{\text{Dihydroxyacetone}}{HCHOH.CO.CH_2OH} \xrightarrow[\text{condensation}]{\text{Aldol}} \underset{\text{DL-Fructose}}{CH_2OH.CHOH.CHOH.CHOH.CO.CH_2OH}$$

(B) **Configuration.** As already stated, D-Fructose gives the same osazone as D-glucose. Hence, the configuration of the three asymmetric carbon atoms of D-fructose must be identical with that of the three asymmetric carbon atoms of D-glucose *not involved in osazone formation*.

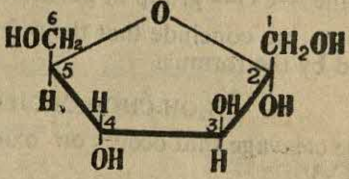


D-Glucose D-Glucosazone D-Fructose

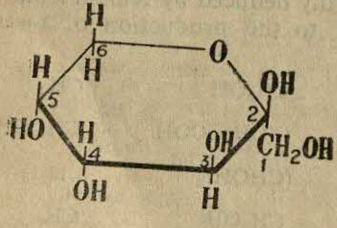
(C) **Pyranose and Furanose Formulae.** D-Fructose is known in both α- and β-pyranose forms, the ordinary fructose being the β-isomer. The pyranose forms pass into the furanose forms more readily than in the case of glucose, and the mutarotation of D-fructose has been shown to be due to the pyranose-furanose conversion. β-D-Fructofuranose is one of the two component units of the sucrose molecule.



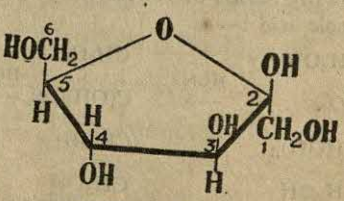
α-D-Fructopyranose
[α]=−21°



α-D-Fructofuranose



β-D-Fructopyranose
[α]=−133·5°



β-D-Fructofuranose

II. DISACCHARIDES

25. **General.**—A disaccharide is a sugar, one molecule of which, on hydrolysis, gives *two* monosaccharide molecules, which may be

identical or different. The four most important disaccharides are *sucrose* (cane-sugar), *lactose* (milk-sugar), *maltose* (malt-sugar) and *cellobiose*. The first two occur as such in nature (the third, *i.e.*, maltose is found free only occasionally). The importance of maltose and cellobiose lies in that they are the product of hydrolysis respectively of starch and cellulose.

The molecular equation for the hydrolysis of the above four disaccharides is :—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

The hydrolysis is catalysed by dilute mineral acids or by enzymes, the latter being specific for hydrolysing a particular disaccharides. The following table gives, in each case, the name of the disaccharide, specific enzyme and the products of hydrolysis :—

Disaccharide	Enzyme	Monosaccharide components
Sucrose	*sucrase* (invertase)	D-glucose and D-fructose
Lactose	*lactase*	D-glucose and D-galactose
Maltose	*maltase*	D glucose (two molecules)
Cellobiose	*cellobiase*	D-glucose (two molecules)

Disaccharides resemble monosaccharides in being sweet, in their solubility and other physical properties.

All the four disaccharides form **octacetates**, showing the presence of *eight* hydroxyl groups in the molecule.

Lactose, maltose, and cellobiose are **reducing sugars**, and closely resemble D-glucose in properties. They are fragmented by alkalis, reduce Fehling's solution, form osazones and glucosides, and show mutarotation.

Sucrose, on the other hand, does *not* possess these properties, and therefore, is a **non-reducing sugar.**

26. Sucrose, *Cane-sugar*, *Saccharose*, *Saccharobiose*, $C_{12}H_{22}O_{11}$, **1-α-D-Glucopyranosido-2-β-D-fructofuranoside.—**

Occurrence. Cane-sugar is economically the most important sugar, and is employed as a sweetening material and food all over the world. It is widely distributed in plants, especially in sugar-cane and sugar-beet. Sugar-cane, originally grown in India, is now cultivated in Java, Cuba, Philippines and other tropical countries. It was at first the only commercial source of cane-sugar. At present, half of the world production of sugar comes from sugar-cane and the other half from sugar-beet, which is grown in temperate climates. The production from beetroot began sometime about the middle of the 18th century in France, mainly as the result of the British blockade of that country during the Napoleonic Wars. The sugar content of the beet has been considerably improved by scientific cultivation, and has steadily risen from about 3 per cent to as high as 15 to 20 per cent, which is the same as that of sugar-cane.

27. Manufacture of Sucrose from Sugar-cane.—The manufacture of cane-sugar from sugar-cane consists of three distinct steps :

(1) **Extraction of juice.** For this purpose the canes are crushed in a cane-mill or a hydraulic press.

(2) **Purification of juice.** The juice contains, in addition to sugar and water, small quantities of vegetable proteins, pectic substances (colloidal carbohydrates) and minerals salts. It must be "defecated" immediately after extraction. If allowed to stand, pectic substances undergo fermentation, producing pectic acids, which catalyse the conversion of cane-sugar into non-crystallizable invert sugar.

The juice, therefore, is at once run into defecator tanks heated by steam coils, and treated with 2 to 3 per cent of lime (**defecation**). By this treatment, the proteins are coagulated and the pectic substances are precipitated as insoluble pectates of calcium. These rise to the surface forming a thick scum, which is removed. The excess of lime is thrown as calcium carbonate by blowing in carbon dioxide (**carbonation**), and the liquid is then filtered. Instead of carbon dioxide, sulphur dioxide is frequently used (**sulphitation**), which yields a liquid of much better colour.

(3) **Concentration and crystallization.** The clarified juice is evaporated to a syrup under reduced pressure in "multiple effect" vacuum pans (Fig. 2). Carbon dioxide is once again passed through the syrupy liquid to decompose any calcium sucrate still present in solution. The precipitated calcium carbonate is filtered off, and the syrup further evaporated *in vacuo* to the crystallization point. The liquid is then run out from the pans and cooled. The crystals are separated from the syrupy mother liquor of "**molasses**" by means of centrifugal machines.

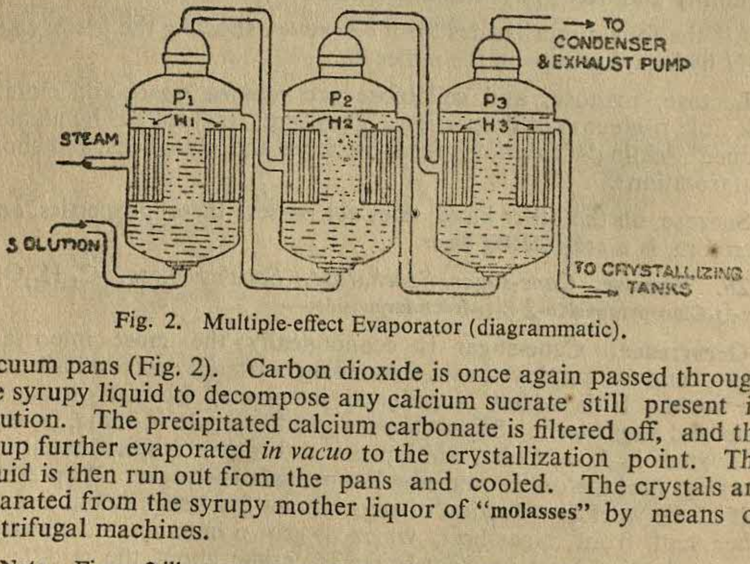


Fig. 2. Multiple-effect Evaporator (diagrammatic).

Note. Figure 2 illustrates the principle of the multiple-effect evaporator. The three evaporating pans P_1, P_2 and P_3, through which the solution to be concentrated is continually circulated and kept at a constant level, are provided with three sets of heating coils. H_1, H_2 and H_3. The pressure in P_1 is highest and that in P_3 lowest. Steam from a boiler is passed through H_1. This makes the liquid in P_1 boil. The steam produced in P_1 passes out into the heater H_2 of the next pan P_2 and is hot enough to keep the liquid in this pan at the boiling point corresponding to the lower pressure prevailing in P_2. The steam produced by the boiling of the solution in P_2 passes into the heater H_3 of the next pan, and makes the solution boil here also. The pressure in this last pan is kept very low by means of an exhaust pump. The saving of the fuel achieved by multiple effect evaporation may be as high as 80 per cent.

28. Manufacture of Sucrose from Beetroot.—Beetroot contains about 15 per cent of sugar, which *it is* not possible to recover by simple pressing. The process employed is known as the **diffusion process**. This is really a process of dialysis, the cell wall acting as a membrane, which allows a free passage of sugar, but not of albuminous and other colloidal matter.

The beets are cut into thin slices, which are then immersed in warm water in vertical tanks, called *diffusers*. Each of these has a capacity of 4,000 to 8,000 litres and is provided with a door at the top for charging it with fresh slices, and another at the bottom for taking out the spent slices (Fig. 3). There is a battery of about 12 diffusers (Fig. 4), arranged either in rows or in a circle, and working on the *counter-current principle*. The liquid enters each diffuser at the bottom and leaves it at the top as shown by arrows in Fig. 3, the slices remaining stationary. The diffuser No. 1 (refer to Fig. 4) into which the fresh water enters, has been longest in action, so that the extraction here is practically complete. It is less complete in No. 2, still less in No. 3, and so on, up to No. 10, which has just been filled with fresh beet slices. The water, after it has passed through diffuser No. 1 thus removing almost the whole of the sugar that the beet contained, passes on to diffusers Nos. 2, 3, 4, etc., until finally the solution having a high sucrose content passes into diffuser No. 10, containing the fresh slices. From here it takes up a further

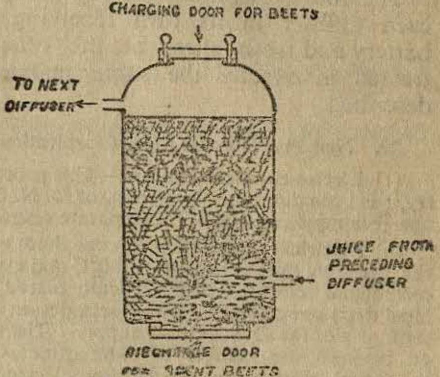


Fig. 3. Diffuser (Vertical Section).

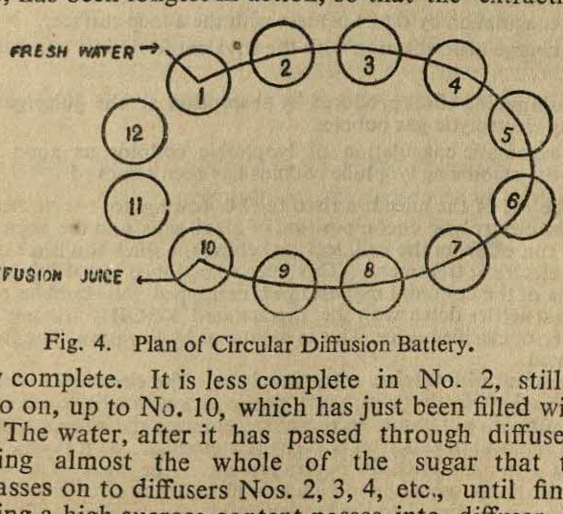


Fig. 4. Plan of Circular Diffusion Battery.

quantity of the sugar, and thus we get a solution having as high a sucrose content as it is possible to get from the beets. This is known as the **diffusion juice**. The waste slices in diffuser No. 12, which previously acted as No. 1, are being removed, while No. 11 which is being filled with fresh slices, will be ready to act as the last diffuser in the following cycle, when No. 2 will become the first diffuser.

The above operations are repeated, round and round the battery, each diffuser in its turn receiving fresh water at one end of the battery and fresh slices at the other end. The diffusion juice is treated in exactly the same manner as the cane juice, as already described.

29. New Processes for Juice Clarification.—

(1) **Electro-chemical Process.**—This process, based on applied colloid chemistry, has been developed by Professor D. N. Ghosh of Patna Science College. The new technique consists of two separate operations detailed below :—

(*a*) **Electrical coagulation of cane Juice colloids.** The raw juice, coming from the crushing mill, is heated to 80°C and electrically treated in specially designed rectangular cells fitted with vertically placed electrodes made of iron sheets insulated from one another. The electrodes at the two ends are connected to the terminals of the D.C. current supply. The total voltage is thus equally distributed between the number of compartments in between the two end plates, each individual sheet acting as a bipolar electrode. To ensure maximum anode area for a given volume of juice the distance between each of the neighbouring plates is kept small (1/8 to 1/2 inch). A voltage range of 1 to 5 volts depending on electrode plate distances, with an average current density of about 0·06 ampere per square inch, brings about coagulation of cane juice colloids in about quarter of an hour without any appreciable rise in temperature. The passage of the current is continued until the *p*H of the juice has risen from 5·4 to 7·0.

From the colloid-chemical point of view, the cane juice consists of a sol in sucrose solution of lyophobic colloids (*e.g.*, mud, fibre, hemicelluloses) stabilized by lyophilic colloids, *e.g.*, pectins and albumens). Almost all the colloids of raw juice carry a negative charge, and their elimination is brought about—

(*i*) by coagulation by direct contact with the anode surface,

(*ii*) by charge neutralization with the trivalent ferric ion generated by anodic corrosion,

(*iii*) by skimming effect produced by absorption at the juice/gas interface of the uprising electrolytic gas bubbles.

(*iv*) by automatic coagulation of lyophobic colloids as soon as the major portion of the stabilizing lyophilic colloids has been removed.

When the *p*H of the juice has risen to 7·0 (owing to deacidification brought about by the electrolytic decomposition of alkali salts and the removal of pectins) the juice is run off from the cell, leaving behind the thick top layer of froth formed during the electrical treatment. This juice when limed to *p*H 8·8 soon cracks of itself ; some of the colloidal material with entrapped gas bubbles rises to the top, while the rest settles down with the precipitated $Fe(OH)_3$ leaving a transparent middle layer of clarified juice. This is separated by filtration. The froth is liquefied and re-treated.

(*b*) **Treatment with calcium superphosphate.** The electrically clarified juice of *p*H=8·8 though perfectly transparent, possesses a yellowish green colour. It gives a positive test with potassium ferrocyanide, showing the presence in it of traces of iron. The removal of this iron is absolutely essential, as it forms highly coloured compounds with nitro-phenolic bodies present in the juice. The alkaline clarified juice is, accordingly, neutralised with a small quantity of calcium superphosphate. On now heating the liquid to the boiling point, a voluminous, flocculent precipitate of calcium pectate and iron and calcium phosphates separates out, which is removed by filtration. The finally clarified juice is neutral, transparent and water-clear, and is directly sent to evaporating pans.

(2) **Ion-exchange Process.** This process of purifying sugar is the most recent one. A report from National Sugar Institute, Kanpur, dated 2nd August, 1960, states that the process is expected to revolutionize sugar production. Besides increasing sugar output by about 10 per cent, it will give edible syrup instead of molasses. The research in this direction has taken the institute four years so far. A pilot plant, costing about Rupees twentyfive lakhs, has already been set up and further work is in progress. As soon as some minor outstanding problems have been solved, the process will be made available to the sugar industry for commercial utilization.

30. By-products of Sugar Industry.—The two chief by-products of sugar industry are :—

(1) **Bagasse.** This is the cellulose refuse of the cane, and is put to the following uses :—

(*i*) As a fuel in the factory.

(*ii*) In the manufacture of "**celotex**"—a building and insulating board.

(*iii*) In the manufacture of low grade paper, lacquers and rayon.

(2) **Molasses.** This is the syrupy mother liquor from which all crystallizable sugar has been recovered, and is used—

(*i*) In the manufacture of alcohol and carbon dioxide.

(*ii*) As a fuel, for which purpose it is atomized with steam and burnt in special burners fitted into a furnace.

(*iii*) As a cattle feed.

31. Properties of Sucrose.—Cane-sugar crystallizes from water in colourless, anhydrous prisms, melting at 160°. It is readily soluble in water (3 parts of sugar in 1 of cold water), but only sparingly so in alcohol. The aqueous solutions are *dextrorotatory*.

When cane-sugar is carefully heated, until it melts, and then allowed to cool, it solidifies to a pale-yellow glassy mass, known as **barley-sugar**. When heated at 200°, it yields a brown product known as **caramel**, which is much used for tinting soups and confectionary.

Reactions.—

(1) **Hydrolysis.** When warmed with dilute acids, sucrose is readily hydrolysed to an equimolecular mixture of glucose and fructose :

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \\ \text{Sucrose} \\ {[\alpha]_D\ +66{\cdot}5^\circ} \end{array} \rightarrow \underbrace{\begin{array}{ccc} C_6H_{12}O_6 & + & C_6H_{12}O_6 \\ \text{D-Glucose} & & \text{D-Fructose} \\ {[\alpha]_D\ +52^\circ} & & {[\alpha]_D\ -92^\circ} \end{array}}_{[\alpha]_D\ -20^\circ}$$

The resulting mixture is *levorotatory*, as the fructose is more strongly levorotatory than glucose is dextrorotatory. Since the solution before hydrolysis was *dextrorotatory*, the process is known as **inversion**, and the mixture of fructose and glucose, so obtained, as **invert sugar**. The invert sugar forms a syrup, which is sweeter than cane-sugar, and is employed for making fruit preserves, *sherbets*, and as a substitute for honey[1].

As already mentioned, sucrose is fermentable by yeast, which contains the enzyme sucrase as well as *zymase*.

(2) **Acetylation.** When boiled with acetic anhydride and sodium acetate, sucrose gives an *octa-acetylsucrose* (m.p 67°).

(3) **Methylation.** When sucrose is treated with methyl sulphate in the presence of alkali, it gives an *octamethyl derivative.*

(4) **Formation of sucrates.** Sucrose forms well-defined metallic derivatives, called *sucrates*. The best known of these is *distrontium sucrate*, $C_{12}H_{22}O_{11}$, 2SrO, which, being sparingly soluble, was once used in the separation of sugar from molasses. With alkali metal hydroxides, sucrates of the type $C_{12}H_{21}O_{11}M$ are obtained.

(5) **Action of concentrated acids.** Concentrated sulphuric acid chars sucrose in the cold, producing carbon, carbon dioxide and sulphur dioxide. Concentrated nitric acid oxidizes it to oxalic acid. Concentrated hydrochloric acid converts it into levulinic acid, $CH_3COCH_2CH_2COOH$.

(6) **Absence of monosaccharide characters.** Sucrose differs from monosaccharides (and from the other disaccharides, mentioned above) in the fact that it **does not react with the carbonyl group reagents** :—

(*i*) It is stable towards alkalis.

(*ii*) It does not react with Fehling's solution or the ammoniacal silver nitrate.

(*iii*) It does not react with hydrogen cyanide, hydroxylamine, and phenylhydrazine.

(*iv*) It does not show mutarotation. The entire absence of these properties shows that the sucrose molecule contains no —CHO or >CO group, free or potential.

32. Constitution of Sucrose.—

(1) The behaviour of sucrose on hydrolysis (reaction 1) shows that the sucrose molecule is built up from one molecule each of D-glucose and D-fructose with elimination of a molecule of water.

(2) The inability of cane sugar to reduce Fehling's solution and to react with the carbonyl group reagents shows that in the formation of the sucrose molecule, the potential —CHO group of the D-glucose and the >CO group of D-fructose are both destroyed. Hence, the linking together of the D-glucose and the D-fructose molecules must have occurred at these two positions (*i.e.* at C^1 of D-glucose and C^2 of D-fructose).

(3) Octamethylsucrose, got by methylation of cane-sugar, when subjected to hydrolysis gives 2,3,4,6-tetramethyl-D-glucose and 1,3,4,

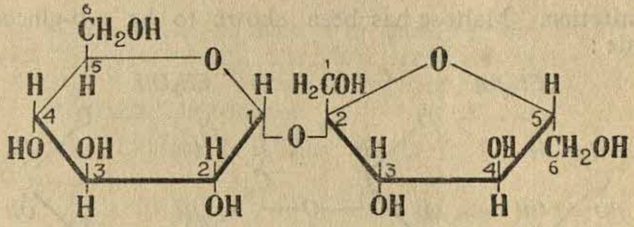
---

[1] Honey is largely invert sugar, which has been manufactured by the bees from sucrose (collected in the form of nectar from flowers) by the action of *invertase* that the bees possess.

6-tetramethyl-D-fructose.[1] Hence, while the D-glucose component of the sucrose molecule has a six-membered or pyranose ring, the D-fructose component has the five-membered or furanose ring.

(4) As to the configuration of the two units, the D-glucose portion is ascribed the α-configuration and the D-fructose portion the β-configuration. This is based on a study of optical rotation and the behaviour towards various enzymes.

For the reasons given above, Hudson has given the full designation of sucrose as 1-α-D-*glucopyranosido*-2-β-D-*fructofuranoside*, which corresponds to the structure :—



α-D-Glucopyranose residue β-D-Fructofuranose residue

33. Synthesis of Sucrose.—The enzymatic synthesis of sucrose from D-glucose-1-phosphate and D-fructose was accomplished by W.Z. Hassid in 1946 with the help of an enzyme obtained from the bacterium *Pseudomonas saccharophila.*

34. Maltose.—*Maltobiose, Malt Sugar,* $C_{12}H_{22}O_{11}.H_2O$.—This sugar occurs in "malt" (sprouted grain of barley) and many other sprouting grains, being produced by the hydrolytic action of the *diastase* of germinating seeds upon starch. It is therefore intimately concerned in the conversion of this insoluble reserve material of plants into soluble sugars, and is an important intermediate product in the manufacture of alcoholic liquors. The *ptyalin* of salvia has a similar action on starch as the *diastase* of germinating seeds.

Manufacture. Starch, made into a thin paste with water, is mixed with about 6 per cent of malt (obtained by allowing moist barley to germinate in the dark at 15°) and the temperature of the mixture kept at about 60°, until the conversion of starch into maltose is complete. The liquid is then boiled to coagulate the proteinous matter, which is filtered off. The filtrate, after being concentrated, may be used to prepare crystals of maltose. But it is more often put on the market as **malt syrup** or **malt extract.**

Properties. Maltose is readily soluble in water, and crystallizes from it in colourless needles having one molecule of water of crystallization. In aqueous solution, maltose undergoes mutarotation, and the specific rotation at equilibrium is $[\alpha]_D = +136°$. Hence it follows that maltose, like, glucose, exists in two forms (α- and β-). The two octaacetates corresponding to these two forms have been prepared.

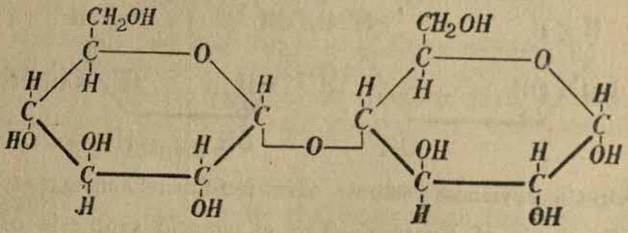
---

[1] This is different from ordinary tetramethyl-D-fructose (obtained from D-fructose itself) which is the 1,3,4,5-compound.

On hydrolysis with dilute acids, or with the enzyme *maltase*, this sugar yields D-glucose. Maltose is fermentable by yeast, the first step in the process being the hydrolysis of the sugar by *maltase* to form glucose ; the latter sugar is then attached by zymase as usual.

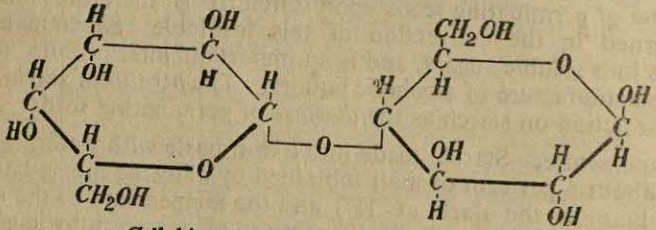
Maltose reduces Fehling's solution, and yields a cyanohydrin, an oxime and an osazone. The latter forms characteristic, needle-shaped crystals which can be readily identified under the microscope.

Constitution. Maltose has been shown to be α-D-glucose-4-α-D glucoside :



This view is in full accord with the chemical properties of maltose given above. Further, this sugar, like α-methyl-glucoside, is hydrolysed by maltase but not by emulsin. Hence it is assigned an α-glucoside structure.

35. Cellobiose.—This sugar is of interest as it is the disaccharide produced by the hydrolysis of cellulose. It closely resembles maltose in chemical properties, and, when hydrolysed yields two molecules of D-glucose. It differs from maltose chiefly in the action of enzymes ; it is hydrolysed by *emulsin* (which is a β-glucosidase) but *not* by *maltase*. Hence it is given a β-glucoside structure :



Cellobiose (β-D-Glucose-4-β-D-glucoside)

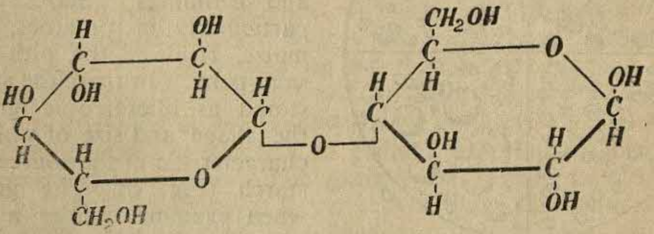
36. Lactose, *Lactobiose, Milk-sugar,* (β-D-glucose-4-β-D-galactose), $C_{12}H_{22}O_{11}.H_2O$.—As its name implies, this sugar is found in the milk of mammals, being present in human milk to the extent of about 7 per cent. Lactose is the characteristic sugar of animals, and in this respect, it offers a complete contrast to sucrose, which is almost exclusively found in plants.

Manufacture. Milk sugar is prepared on a large scale from cow's milk, which contains about 4·5 per cent of this sugar. The whey obtained as a by-product in the manufacture of cheese or casein from milk, is evaporated to crystallization in vacuum pans. The crude product thus obtained is purified by recrystallization from water, a little animal charcoal being used to bring about decolorization.

Properties. Lactose, like maltose, crystallizes from water with $1H_2O$. It exhibits muta-rotation, and the specific rotation at equilibrium is $[\alpha]_D = +55{\cdot}3^\circ$. Hence, lactose exists in two forms, α- and β-.

Lactose closely resembles maltose in chemical properties. When hydrolysed with dilute acids, it yields a molecule of D-glucose and β-D-galactose. It reduces Fehling's solution, and yields a cyanohydrin, an oxime and an osazone.

Constitution. Lactose has been shown to be **β-D-glucose-4-β-D-galactose:**



β-D-Galactose unit β-D-Glucose unit

The above structure is supported by the chemical behaviour of lactose and by the fact that it is hydrolysed by the enzyme *emulsin* and not by *maltase*.

Uses. (1) Large quantities of milk sugar are used in medicine, especially by homoeopathic and biochemic physicians.

(2) It is added to cow's milk given to babies, in order to supply the deficiency of this constituent.

(3) It is also used in the silvering of mirrors.

(4) Since lactose is not directly fermentable by ordinary yeast, it is sometimes used in brewing. Being left unchanged, it improves the flavour of the beer.

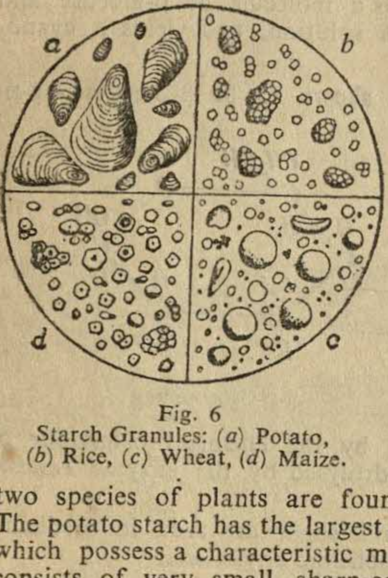
(5) Lactose can be fermented by the yeast of Caucasian kephir grain, which contains *lactase* as well as *zymase*. *Koumiss*, an alcoholic beverage used in Russia, is made in a similar manner by fermenting mare's milk.

III. POLYSACCHARIDES

37. General Characteristics.—Like the disaccharides, the polysaccharides are regarded as the anhydrides of monosaccharides, being formed from *n* monosaccharide molecules by elimination of

$n-1$ molecules of water. Hence, the general formula of the polysaccharides is $(C_6H_{10}O_5)_n.H_2O$. The value of n varies from 12 to about 200.

Polysaccharides are tasteless amorphous compounds, some of which are insoluble in water, while the others form colloidal solutions and gels. On being hydrolysed by hot dilute acids, or enzymes, they yield monosaccharides, often forming disaccharides as intermediate products. Polysaccharides form acetyl derivatives and nitric esters, showing that their molecules contain hydroxyl groups.



38. **Starch** (*amylum*).—Next to cellulose, starch is the most abundant material found in the vegetable kingdom. In plant metabolism, starch occupies a central position among the carbohydrates, being transformed by enzyme action either into the simpler mono- and disaccharides, or into the more complex gums and celluloses. Starch occurs particularly in potatoes, wheat, maize, rice and the pith of the sago-palm. In these the starch is stored as microscopic granules, the shape and size of which are characteristic of the source of the starch (Fig. 6). The granules, when examined under a microscope, are found to consist of an inner nucleus, or "hilum," around which are arranged a number of concentric layers or "striae". No two species of plants are found to give exactly identical starches. The potato starch has the largest granules (0·05 to 0·1 mm. diameter) which possess a characteristic mussel-like appearance. Rice starch consists of very small, sharp-cornered granules, having almost a crystalline appearance (0·003 to 0·007 mm. diameter). They have a tendency to collect together to form large granules. Wheat starch consists of round, lens-shaped granules of 0·02 to 0·03 mm. diameter, while maize starch consists of characteristic polyhedral granules with a dark centre and no visible striae.

Manufacture. Starch manufacture is a very important industry. The two largest starch producing countries of the world are Germany and America. In Germany, starch is manufactured chiefly from potatoes, and to a smaller extent from rice, while in America the chief source is maize. In India, Great Britain and other countries both wheat and rice are employed for this purpose.

The manufacture of starch is essentially a process of mechanical separation from other materials with which it is associated. The procedure adopted differs in individual cases.

In the case of potatoes, after preliminary washing to remove earth, sand and grit, the tubers pass to a rasping machine in order to rupture the cells. The pulp thus obtained is carried by a fine stream of water on to fine-mesh brass sieves, to separate the starch from coarser particles and fibrous material. The resulting milky liquid is run into settling tanks to separate fine sand and grit. It is then allowed to run slowly over long, shallow, wooden troughs, or gutters where the pure starch settles out while the aqueous liquid, along with the impurities, passes off. The pure white starch is washed from the gutters by a steam of cold water, and is pumped through filter presses. The starch thus obtained is in the form of a cake containing about 40 per cent of water.

In rice and other cereals, the starch is associated with varying proportion of protein or gluten material which must be separated from starch. The protein present in rice is rendered soluble by very weak caustic soda solution. This fact is utilized in the production of starch from rice.

In the case of wheat, the gluten forms an elastic mass with water which it is not possible to remove by levigation. Hence, in this case, the grain is first ground into flour, which is then made into a dough with water. This is spread on a fine brass sieve where a moving roller presses out the starch, which is levigated off by a spray of water. The resulting milky liquid is then treated as usual.

Maize contains, in addition to protein, a germ rich in oil, which it is necessary to separate. The grain is first steeped for 2 or 3 days in warm water containing 1 per cent of SO_2. It is then ground in stone mills, and resulting pasty mass is stirred up with water. The suspension is passed through a large, V-shaped tank provided with a screw conveyer at the bottom, and skimming paddles at the top. The germ of the maize floats, and is skimmed off by the paddles. The starchy and dextrinous matter passes on in the liquor. This is delivered over a series of sieves which retain coarser particles, bran, and fibre, while a milky liquid, containing starch cells, passes through. From this the starch is recovered in the same manner as described in the case of potatoes.

The final drying of the starch cake, obtained from any one of the above sources, must be carried out at as low a temperature as possible to prevent the gelatinization of the starch granules. In the tropics, the drying is usually carried out in the open air, while in Europe and America it is effected in a current of warm dry air, or by evaporating off the moisture in vacuum chambers.

Properties.

(1) *Physical Characters.* Starch is a white, hygroscopic powder, without any taste or smell. The starch granules really consist of two very similar polysaccharides : (*i*) **amylose**, or true starch, which is present in the interior of the granules and is soluble in water, and (*ii*) **amylopectin**, which is the surrounding part of the starch granules and swells up to form a gel with water. As already described, the

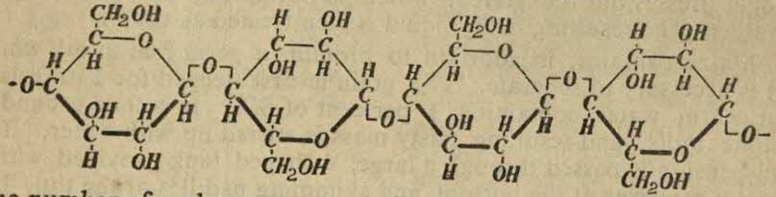
granules of starch from different plants are of different characteristic shapes and sizes.

(2) *Reaction with Iodine*. The amylose[1] content of starch (**soluble starch**) gives a pure blue colour with iodine. This is employed as a **characteristic test** both for iodine and starch. The colour appears to be due to the adsorption of iodine by starch, and not to the formation of a compound.

(3) *Hydrolysis*. When boiled with dilute acid, starch is hydrolysed, yielding a number of simple polysaccharides (collectively known as **dextrins**), then the disaccharide maltose, and finally D-glucose. Short of complete hydrolysis to D-glucose, the products are mixtures of variable composition depending on the nature and duration of treatment.

(4) *Action of Nitric Acid*. When treated with a mixture of concentrated nitric and sulphuric acids, starch gives **nitro-starch**, which is a mixture of nitric esters (compare nitro-celluloses). Nitro-starch is used as a **blasting explosive.**

Structure. The starch molecule has been shown by Haworth and co-workers to consist of a chain of α-D-gluco-pyranose units linked together through oxygen atoms, at carbon atom 4, as in the maltose formula. A small portion of the starch formula is shown below :—



The number of α-glucopyranose units in the molecule of starch is about 28. Hence the molecular weight is of the order of 5,000.

Industrial Uses of Starch.

(1) *As Food*. Starch is one of the essential constituents of our food. Its function is chiefly the production of bodily heat. We use starch in the form of corn-flour, arrow root, sago, *sooji*, and as a constituent of bread, rice, potatoes and many other food articles.

(2) *As a source of Glucose and Alcohol*. Starch finds extensive application in the manufacture of "starch syrup", "corn syrup", glucose and alcohol.

(3) *As an Adhesive*. Starch jelly is much used in bookbinding and for other purposes. Commercial **dextrin** or **British gum** (manufactured by heating starch with 1 per cent solution of nitric acid, using low-pressure steam) is the adhesive used on postage stamps, envelopes and paper labels.

(4) *In Laundries*. Rice starch is extensively used by washermen for stiffening linen. The gelatinized starch is applied to the cloth, and is converted by ironing into a shiny stiff layer of dextrin.

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[1] Amylopectin, on the other hand, gives a violet colour with iodine.

39. Cellulose.—Cellulose is the most complex polysaccharide known. It is very widely distributed in the vegetable kingdom, and forms the fundamental constituent of walls of plants and skeletons of all vegetable tissues. Cotton, jute, hemp, flax, paper, wood, etc., are all different forms of cellulose containing small amounts of mineral matter which is left behind when these substances are burnt.

Preparation. Pure cellulose may be obtained from cotton-wool, flax or paper. The material is treated successively with dilute hydrochloric or hydrofluoric acid (to remove mineral matter, water, alcohol, and ether). The cellulose, which is very stable towards dilute acids and alkalis, is thus obtained as a pure white, amorphous mass.

Cotton and linen cloths consist entirely of cellulose. The finest Swedish filter paper, got by extracting ordinary filter paper with hydrofluoric acid, is almost a chemically pure form of cellulose.

Properties.

(1) *Physical Characters.* Cellulose like starch, possesses an organised structure, and occurs in the form of **hollow fibres**, the appearance and dimensions of which are characteristic of their particular source. It is because of this structural peculiarity that cellulose forms the basis of the paper and the textile industries.

(2) *Solubility.* Cellulose is insoluble in all the ordinary solvents, but dissolves in **Schweitzer's reagent** (ammoniacal solution of cupric hydroxide), forming a colloidal solution, from which the cellulose may be recovered as a gelatinous precipitate by the addition of an acid. Cellulose is also soluble in a solution of zinc chloride in hydrochloric acid.

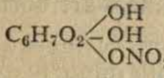
(3) *Hydration.* When cellulose is treated with dilute acids or comminuted mechanically with water (as in paper making), it is converted into a hydrated cellulose or **hydrocellulose**. The hydration of cellulose is of great importance in plant physiology, since it determines the conditions of equilibrium between the water content of the cell wall and the sap. It also plays an important role in the seasoning of timber.

(4) *Hydrolysis by Concentrated Acids.* When cellulose is treated with cold concentrated sulphuric acid, it swells up and passes gradually into solution. On adding water to this solution, a starch-like substance, called **amyloid**, is precipitated. When hydrolysed with sulphuric acid, cellulose first yields **cellodextrins** (which resemble the dextrins obtained from starch), then the disaccharide **cellobiose** and finally glucose.

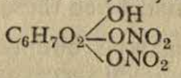
(5) *Action of Alkalis.* Though cellulose is remarkably resistant to dilute alkalis, with a 15 to 20 per cent solution of caustic soda its ribbon-like fibre, having reticulated walls, swells up into a smooth-walled cylinder. This fact was noted in 1884 by John Mercer. H.A. Lowe, in 1889, observed that if a cotton fabric, while immersed in alkali, be subjected to simultaneous stretching to counteract the contraction consequent on the swelling, it acquires a characteristic

silky lustre. The process is known as **mercerization**, and is employed industrially on a large scale.

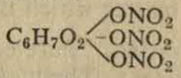
(6) *Esterification*. The cellulose unit, $C_6H_{10}O_5$, behaves as a **trihydric alcohol**, and, like glycerol, gives three series of ester. Thus with nitric acid it forms mono-, di-, and trinitrates :



$C_6H_7O_2\left\langle\begin{matrix}OH\\OH\\ONO_2\end{matrix}\right.$



$C_6H_7O_2\left\langle\begin{matrix}OH\\ONO_2\\ONO_2\end{matrix}\right.$



$C_6H_7O_2\left\langle\begin{matrix}ONO_2\\ONO_2\\ONO_2\end{matrix}\right.$

(*a*) *Cellulose Nitrates*. When cellulose is treated with a mixture of concentrated nitric and sulphuric acids, the above three products are obtained. The degree of esterification depends upon the quantity of the acid mixture used, the temperature, and time allowed for the reaction to proceed. Two important types of "cellulose nitrates", (*i.e.*, mixture of the above esters in varying proportions) are manufactured on a large scale. These are : (1) **pyroxylin** or **collodion cotton**, which consists mainly of the dinitrate, and (2) **gun-cotton**, which consists almost entirely of the trinitrate. Cellulose nitrates retain the fibrous structure of cellulose.

(*b*) *Cellulose Acetates*. When treated with a mixture of acetic anhydride and glacial acetic acid, together with about 10 per cent of sulphuric acid (to act as catalyst), cellulose is converted into mixture of di- and tri- acetates. These are much used in the manufacture of **artificial silk** and **cellulose paints**.

40. Industrial Applications of Cellulose.—Industrially, cellulose is the most important of all organic substances, and ours is the age of cellulose as much as of iron and steel. Thus, some of the more important applications of cellulose materials are :

(1) **Textile Industry.** Cellulose, in its natural fibrous form, finds extensive application in the manufacture of cotton and linen textiles. The lower grades of cotton and flax, and more particularly jute are employed for making wrapping, gunnies and mattings. Cereal straws, canes and bamboo are used for making hats, basket-work, coir, etc.

(2) **Paper Manufacture.** Formerly, paper was manufactured almost exclusively from linen rags. At the present day it is prepared mainly from wood pulp, esparto grass, *bhabhar* grass, and corn stalks. In making inferior grades of paper, such as those meant for newspapers, wrapping, etc., **mechanical wood-pulp** is used. This is obtained from pine and other soft woods by a process of mechanical grinding in the presence of water, and thus consists principally of lignocellulose of the original wood. Such paper is difficult to bleach, and turns yellow with age. It is, therefore, unfit for the printing of books and for other works of a permanent nature. For such purposes **chemical wood-pulp**. consisting of pure cellulose, is employed. This is obtained by digesting under pressure the disintegrated wood with either (*i*) a solution of calcium bisulphite (*Sulphite Process*) or (*ii*) a dilute solution of sodium hydroxide (*Caustic Soda Process*). By these treatments, the "incrusting" lignin of lignocellulose passes into

solution, and a fibrous, more or less pure cellulose is left. This is known technically as "*half-stuffs*" and, after being bleached and washed, is made into paper.

The cellulose material obtained as above is beaten into a pulp with water, and run on to an endless band of exceedingly fine wire-gauze, which, along with the web of paper upon it, passes between rollers covered with felt. The gentle pressure exerted by the rollers causes the removal of much water, and renders the paper compact. The paper now leaves the wire gauze, and passes on to a continuously revolving band of woollen felt, and is subjected to a further pressure between rollers. From the press-rolls the paper passes to the steam-heated drying and polishing cylinders, where it receives a fine glaze. Finally it is wound on reels.

(3) **Explosives.** Mixture of cellulose nitrates, containing a high proportion of the trinitrate, are extensively employed both as *high* (disruptive) and *low* (propellant) explosives. The almost fully nitrated cellulose, called **gun-cotton**, can be detonated even when damp, and in the form of compressed blocks, is employed for charging torpedoes and submarine mines. The explosion is extremely terrific, being about 500 times more violent than that caused by gun powder. A mixture of gun-cotton with nitroglycerine and vaseline, known as **cordite**, is employed as a propellant.

(4) **Artificial Silk.** Cellulose is now very extensively employed in the manufacture of artificial silk or **rayon.** The process consists essentially in forcing a syrupy solution of cellulose, or a cellulose derivative, through fine apertures into a warm chamber, or a suitable bath. By this means, the solvent is removed, and the cellulose, or the derivative, is obtained as fine threads, which are twisted or wound on bobbins to be woven subsequently into cloth. There are four different processes for the manufacture of artificial silk.

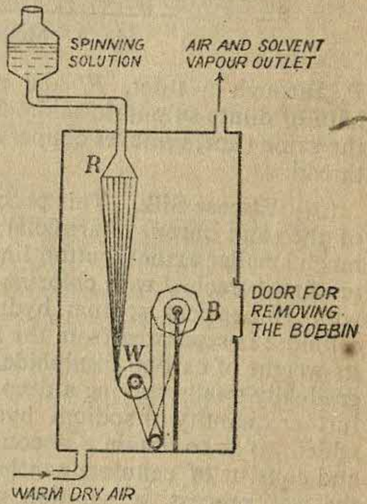


Fig. 7. Method of Dry Spinning.

(*i*) **Chardonnet Silk (Nitrocellulose Rayon).** In this process, *collodion*, which is a colloidal solution of collodion cotton in a mixture of alcohol (1 vol.) and ether (3 vols.) is ejected, through a rose-nozzle *R* (Fig. 7), as a bundle of separate filaments. These are dried by a current of warm dry air, passing upwards, which carries the solvent vapour away through the outlet at the top of the Chamber. The filaments, on passing round the pulley wheel, *W*, converge, and the resulting yarn gets wound on the bobbin, *B*, which can be removed through a door in the front part of the chamber.

Since nitrocellulose is highly inflammable and explosive, it is necessary to *denitrate* the spun material, and thus convert it back into cellulose. This is effected by dipping the material in a reducing bath of sodium hydrogen sulphide, NaSH, or ammonium hydrogen sulphide, NH_4SH. The denitrated yarn is then woven into cloth.

(*ii*) **Cuprammonium Silk.** In this case, a solution of cotton linters or of sulphite wood pulp in Schweitzer's reagent is forced by a pump *P*, through a filter, *F*, and a spinnerette, *S* (Fig. 8), into a setting bath of dilute sulphuric acid. This coagulates the filaments and, at the same time, removes copper and ammonia, giving a pure cellulose thread.

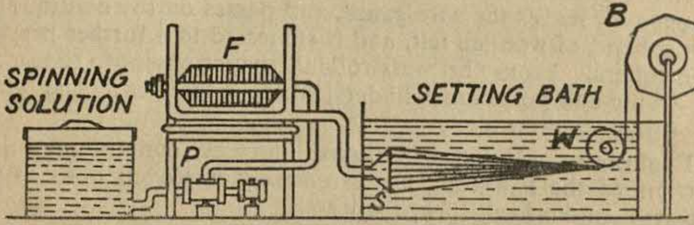


Fig. 8. Method of Wet Spinning.

(*iii*) **Viscose Silk.** This process is responsible for over 80 per cent of the total output of artificial silk. Bisulphite wood pulp and, to a much smaller extent, cotton linters are the starting materials. They are first bleached with chlorine and then mercerized for two hours with 16 per cent sodium hydroxide solution. The resulting alkali cellulose is separated from the liquid and treated with 60 per cent of its weight of carbon disulphide. In 3 to 4 hours' time the product gradually swells, giving a deep orange-coloured gelatinous mass. A further quantity of sodium hydroxide solution and water are now added, so as to obtain a viscous solution. This is known as **viscose**, and consists of cellulose xanthates. Viscose is filtered and spun by the wet process, a solution of sulphuric acid and sodium sulphate being used as the congealing medium.

(*iv*) **Acetate Silk.** In this process cotton linters are treated with a mixture of acetic anhydride, glacial acetic acid and a little sulphuric acid. The whole of the cellulose acetate is precipitated by pouring it into water. The acetate is filtered, washed, dried and finally dissolved in acetone. The solution is spun by the dry process, most of the solvent being recovered by refrigeration and used once again.

All the **rayons differ from natural silk** in the fact that they contain no nitrogen. Natural silk is a protein material, and can be readily distinguished from artificial silk by burning it, when it shrinks into a ball of cinder emitting an odour of burnt hair.

(5) **Films.** Transparent films are prepared according to the same general principle as artificial silks. Suitable solutions of cellulose

derivatives are passed through fine slits or spread on warm plates. Collodion films are very inflammable, while viscose films are practically non-inflammable. Thin tissue of viscose, known technically as **cellophane**, is used for making wrappers, wall papers, imitation tapestries, and in many other ways. Corked bottles are hermetically closed by viscose caps. The so-called **safety glass** is a two or three ply material made by cementing sheets of glass by collodion or viscose film.

(6) **Lacquers.** Lower nitrates of cellulose, dissolved in special solvents with special thinners and suitably pigmented, are applied to motor car bodies by means of a brush or a sprayer. Similarly, the acetone soluble cellulose acetates are employed for imparting a shrunk, water-proof finish to aeroplane wings and textile fabrics.

(7) **Celluloid.** (*Artificial Ivory or Xylonite*). This is one of the best known synthetic plastics, and is manufactured by incorporating collodion cotton with camphor in the presence of suitable solvents, such as alcohol or amyl acetate. It is transparent and colourless, or slightly yellowish, and can be tinted with the most delicate colours. When immersed in water at about its boiling point, celluloid becomes plastic, and can be moulded into any desired form. Further, at the ordinary temperatures, it can be cut, turned and drilled, and is employed in the manufacture of numerous useful and ornamental articles such as watch cases, knife handles, paper cutters, combs, toys, etc.

QUESTIONS

1. Describe the constitution of glucose and state clearly in what respects do glucose and fructose resemble an aldehyde and a ketone respectively. Why do we believe that these do not contain CHO and CO groups ? (*Rajasthan, B.Sc., 1962*)

2. (*a*) What are carbohydrates ? What is their importance in everyday life?
   (*b*) Describe in brief the viscose process for manufacturing artificial silk. (*Allahabad, B.Sc., 1954*)

3. In what respects are the aldohexoses and ketohexoses similar to each other and to simple aldehydes ? In what respects do the three classes of compounds differ ? (*Rajputana, B.Sc., 1950*)

4. Discuss the constitution of Fructose. (*Lucknow, B.Sc., 1962*)

5. How is the configural formula of arabinose arrived at ? How will you convert arabinose to glucose, and glucose to fructose ? (*Bombay, B.Sc., Chemistry, Subs., 1963*)

6. Give the preparation of glucose on a large scale. Discuss its structural formula. How would you convert glucose into fructose ? [*Bombay, B.Sc., Chemistry (Subs.), 1961*]

7. How do you arrive at the structure of glucose ? What are nitrocelluloses ? Give examples. (*Calcutta, B.Sc., 1962*)

8. Describe the constitution of glucose and state clearly in what respects do glucose and fructose resemble an aldehyde and a ketone respectively. Why do we believe that these do not contain CHO and CO groups ? (*Ajmer, B.Sc., 1962*)

9. Discuss briefly the experimental evidence that led to the adoption of the constitutional formula of glucose. How is glucose converted into fructose ? (*Gauhati, B.Sc., 1962*)

10. How are Carbohydrates classified ? Mention the important properties of monosaccharides. How can Glucose be transformed into fructose and fructose into glucose ? (*Andhra, B.Sc., 1962*)

11. How would you convert an aldose to a ketose and vice versa ? Deduce the constitution of Glucose. (*Madras, B.Sc., 1962*)

12. Discuss the constitution of Sucrose.

Discuss the reactions by which you may distinguish between Dextrose, Laevulose, and Sucrose. (*Punjab, B.Sc., 1962*)

13. Give a general classification of carbohydrates and show their inter-relationship. Explain the following conversions :

$$\text{Glucose} \rightleftharpoons \text{Fructose}$$
$$\text{Glucose} \rightleftharpoons \text{Arabinose}$$

(*Bombay, B.Sc., Chemistry, Subs., 1962*)

14. Discuss the configuration of Fructose. Give evidence in support of its ring structure. Show how fructose is converted into glucose. (*Bombay, B.Sc., 1959*)

15. How can glucose be obtained from a polysaccharide ? In what ways does glucose differ from fructose and sucrose ?

Does glucose possess an aldehyde or a ketone group ? Give at least four reactions to prove your statement. (*Calcutta, First M.B.B.S., 1959*)

16. Explain what you understand by the term '*aldohexose*' and '*ketohexose*'. Does an osazone obtained from an aldohexose differ from that obtained from a ketohexose ? Give reasons for your answer.

By what tests, both physical and chemical, would you proceed to differentiate an aldose from a ketose ? (*Calcutta, First M.B.B.S., 1960*)

17. Write an essay on carbohydrates. (*Lucknow, B.Sc., 1962*)

18. (*a*) What are carbohydrates ? What are their uses in daily life ?
(*b*) Discuss the structure of *d*-glucose. (*Lucknow, B.Sc., 1960*)

19. Illustrate the methods of ascending and descending the sugar series, and also the interconversion of aldoses and ketoses. (*Madras, B.Sc., 1960*)

20. How is the structural formula of glucose arrived at ? How is glucose converted into fructose ? (*Poona, B.Sc., 1960*)

21. Discuss the configuration of glucose and furnish evidence in favour of its pyranose ring structure. (*Karnatak, B.Sc., 1960*)

22. Describe the manufacture of cane sugar and state its properties and uses. How would you distinguish between glucose and cane sugar ? (*Calcutta, B.Sc., 1960*)

23. Discuss the structure of glucose. How can it be converted into fructose ? (*Nagpur B.Sc., 1960*)

24. How does glucose occur in nature ? Outline the present-day views on the structure of glucose. How would you convert it into fructosazone ? (*Delhi, B.Sc., 1960*)

25.* Establish the presence of an aldehyde group in glucose. How will you distinguish glucose from fructose ? How is glucose converted to fructose and *vice versa*. (*Jabalpur, B.Sc., 1960*)

26. Write a note on osazone formation. (*Punjab, B.Sc., 1963*)

27. Discuss in detail the structure of glucose. (*Punjab, B.Sc., Chem. Eng., 1963*)

28. How is glucose prepared ? How is its structural formula arrived at ? How is glucose converted into fructose ? (*Poona, Second Year, B.Sc., 1961*)

29. How will you obtain ?
(*a*) Fructose from glucose,
(*b*) Glucose from fructose,
(*c*) Glucose from arabinose,
(*d*) Arabinose from glucose. (*Lucknow, B.Sc., 1959*)

PART III

CYCLIC OR CLOSED CHAIN COMPOUNDS

CHAPTER THIRTY-FIVE

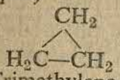
ALICYCLIC COMPOUNDS

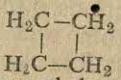
1. Classification of Cyclic Compounds.—As already mentioned the cyclic compounds are divided into two main groups : (1) **carbocyclic** and (2) **heterocyclic**. In the former, the rings are composed entirely of carbon atoms, while in the latter, they contain, in addition to carbon, one or more atoms of a polyvalent element.

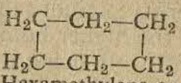
The carbocyclic compounds are sub-divided into two classes : (1) **alicyclic compounds**, and (2) **aromatic compounds**. The former class possess the usual characters of saturated or unsaturated aliphatic compounds according to the nature of the links present, while the latter class is characterized by a number of properties, the so-called *aromatic characters*, which sharply mark them off from the aliphatic compounds.

In this chapter, we shall discuss the alicyclic compounds, while the aromatic compounds will be taken up in the following chapters. Alicyclic compounds containing rings of *six* carbon atoms are related to certain aromatic compounds, and for that reason, are, termed **hydroaromatic compounds.**

2. Cycloalkanes or Cyclanes, C_nH_{2n}.—Saturated hydrocarbons containing *one* ring form a homologous series with the *general formula* C_nH_{2n} (the same as for alkenes). They are called **cycloalkanes**, **cycloparaffins** *or* **polymethylenes.** Two systems of naming this series of hydrocarbons are in uses. In one of these, they are termed *tri-*, *tetra-*, etc., *methylenes*, according to the number of CH_2 groups in the ring. In the other, the Geneva system, they are named after the corresponding alkanes by adding the prefix cyclo- to the alkane name. For example,


Trimethylene or cyclopropane


Tetramethylene or cyclobutane


Hexamethylene or cyclohexane

Cyclanes with 3 to 34 carbon atoms in the ring are known. Those containing 5- or 6-membered rings are important components of petroleum, and in the petroleum chemistry they are usually called **naphthenes**[1] ; *e.g.*,

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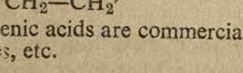
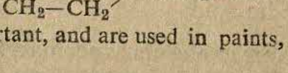
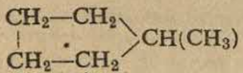
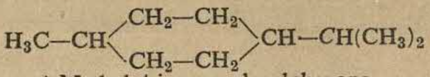
[1] Caucasian petroleum contains considerable quantities of naphthenes and also about 1 per cent of monocarboxylic **naphthenic acids**, *e.g.*,


and


The naphthenic acids are commercially important, and are used in paints, timber preservatives, etc.



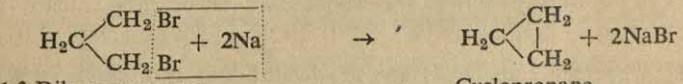
Methylcyclopentane
(C_6H_{12})



1-Methyl-4-isopropylcyclohexane,
($C_{10}H_{20}$)

3. Preparation of Cyclanes and their Derivatives.—The methods used in preparation of cyclanes and their derivatives include (*i*) Cyclization or ring closure and (*ii*) hydrogenation of aromatic rings. The following are the more important methods for preparing cyclanes.

(1) **Dehalogenation of dibromo-** *or* **dichloroalkanes** (*Freund's Reaction*). When a dibromo- or dichloro-alkane is treated with sodium or zinc, cyclization of the carbon chain occurs ; *e.g.*,

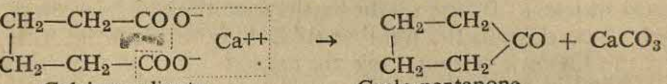


1,3-Dibromopropane Cyclopropane

This method is really an extension of Wurtz synthesis and was employed by Freund (1882) in preparing cyclopropane by the action of sodium on trimethylene bromide. Gustavson, in 1886, showed that the yield could be improved to about 70 per cent by using zinc dust and alcohol instead of sodium.

Cyclization by this method occurs most readily with 1,3-dihalogen compounds. The yield decreases with the size of the ring, being as low as 40 per cent for cyclohexane. The method is practically useless for producing larger rings.

(2) **From adipic acid and higher homologues.** This is a very general reaction by which cyclic compounds having 5 to 29 carbon atoms in the ring have been prepared. Thus, calcium adipate when submitted to dry distillation yields cyclo-pentanone ;



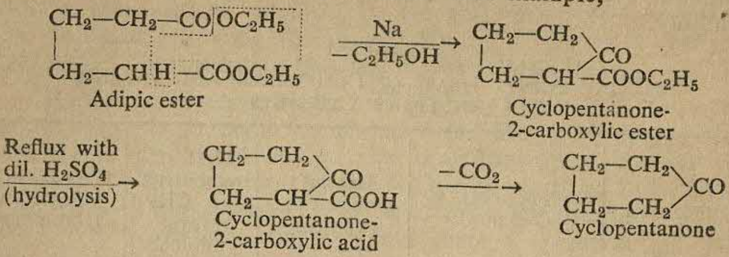
Calcium adipate Cyclo-pentanone

Formerly, calcium salts alone were used for this purpose, but the yields of the higher homologues, from cyclononanone onwards, were very small. By using thorium salts Ruzicka has been able to obtain cycloketones having up to 29 carbon atoms in a closed chain. These may be converted into corresponding cyclanes by reduction with zinc amalgam and concentrated hydrochloric acid (Clemmensen reduction, p. 275).

(3) **By malonic ester synthesis** (*Perkin's method*). Carboxylic acids derived from cyclo-paraffins may be obtained by the action of dibromo-paraffins on the disodio-derivative of malonic-ester (page 383, reaction 6). The monocarboxylic acids thus obtained may be converted into the corresponding cyclo-paraffins by reduction with hydriodic acid.

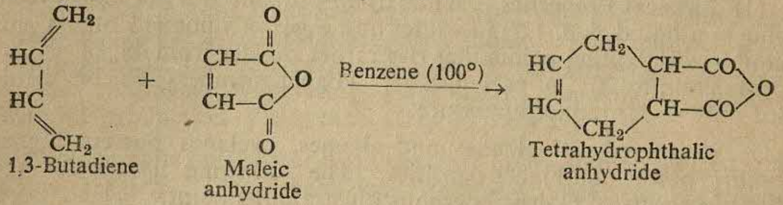
(4) **Intramolecular acetoacetic ester condensation.** (*Dieckmann's method*). This is an excellent general method for preparing 5- or 6-membered ring compounds, and consists in treating an appropriate

dicarboxylic ester with metallic sodium. For example,


Adipic ester
Na
$-C_2H_5OH$
Cyclopentanone-2-carboxylic ester
Reflux with dil. H_2SO_4 (hydrolysis)
Cyclopentanone-2-carboxylic acid
$-CO_2$
Cyclopentanone

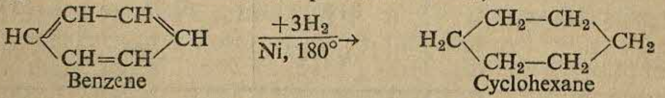
The resulting ketone may be converted into the parent cyclane by the Clemmensen reduction (p. 275).

(5) **Diels-Alder reaction.** This very important reaction was discovered by Prof. Otto Diels of the University of Kiel and his associate Kurt Alder in 1928, who, 22 years later (1950), were awarded the **Nobel Prize** in chemistry in recognition of numerous important applications of the reaction. It consists in **1,4-addition of a conjugated diene** to a second component having a C=C bond flanked by CO, COOH or CN groups. Thus, 1,3-butadiene and maleic anhydride, when heated together (in benzene solution) at 100°, give a quantitative yield of tetrahydrophthalic anhydride :—



All conjugated dienes undergo Diels-Alder reaction, and maleic anhydride may be replaced by any other compound containing an ethylenic bond activated by neighbouring strongly electronegative group or groups.

(6) **Hydrogenation and aromatic compounds:** A very important source of 6-carbon cyclanes and their derivatives is the catalytic hydrogenation of aromatic compounds. Thus,



Similarly, toluene (methylbenzene) and 1,3-dimethylbenzene give methylcyclohexane and 1,3-dimethylcyclohexane respectively. Benzoic acid and phthalic acid give the corresponding cyclohexanecarboxylic acids.

4. Properties of Cyclanes.—In the following table are given some of the constants of cyclanes. Ethylene, though not generally taken as a cyclane, is included in the table, as the double bond of its molecule may be regarded as the limiting case of a cyclane ring with maximum tendency to open up, and thus serving as a standard of instability.

TABLE I

BOILING POINTS, HEATS OF COMBUSTION AND VALENCE ANGLES OF CYCLANES

Hydrocarbon	Boiling point °C (760 mm)	Heat of combustion (kilo-cal)	Heat of combustion per CH_2 group (kilo-cal)	Deviation of valence angle from normal
C_2H_4	−104	338	169	+54°44′
C_3H_6	− 33	504	168	+24°44′
C_4H_8	+ 12	664	166	+ 9°44′
C_5H_{10}	49	798	159	+ 0°44′
C_6H_{12}	81	940	157	− 5°16′
C_7H_{14}	117	1100	158	− 9°33′
C_8H_{16}	145	1260	158	...
$C_{12}H_{24}$	118°/18 mm	1884	157	...
$C_{22}H_{44}$	212°/16 mm	3424	156	...
$C_{30}H_{60}$	230°/0·2 mm	4680	156	...

(1) **Physical Properties.** While cyclo-propane is a gas and cyclobutane a liquid (*b.p.* 12°) in winter and a gas in summer, others are liquids with boiling points that rise rather rapidly from 49° of cyclopentane up to 201° of cyclodecane. Higher members can be distilled only under reduced pressure.

As compared with alkanes, and alkenes, cyclanes possess higher boiling points and higher densities. The following figures for the boiling points of C_6-hydrocarbons illustrate the point.

TABLE II

COMPARISON OF BOILING POINTS AND DENSITIES OF CYCLANES WITH ALKANES AND ALKENES

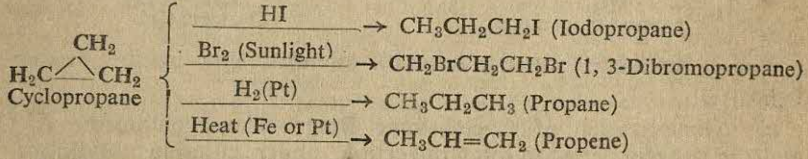
	Cyclohexane	*n*-Hexane	Hexene-1
Boiling point (760 mm)	84·8°	68·8°	63·9°
Sp. gr. (20°/4°)	0·7787	0·6504	0·6736

Like other hydrocarbons, cyclanes are insoluble in water and soluble in alcohol and ether.

(2) **Ring Size and Stability.** The last two columns of Table I are very instructive, as they bring out, in a striking manner, the relationship between stability and the size of the cyclane rings. The heat of combustion per CH_2 group decreases up to cyclopentane, showing that the stability of the ring is on the increase. This is in full accord with the deviation of valence angle from the normal as

calculated from **Baeyer's strain theory** (page 70). From cyclohexane onwards the heat of combustion per CH_2 group becomes practically constant, showing the inapplicability of Baeyer's theory to larger rings. This is fully explained by **Sachse-Mohr theory** (page 71).

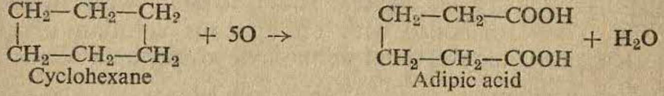
(3) **Rupture of Cyclane Rings.** The figures in the last column of Table I, which have been calculated from Baeyer's theory, reveal considerable strain (24°44′) in the three-membered carbon ring. Though much less than that of the double bond, it is quite high as compared with bigger rings. For this reason, cyclopropane behaves more like ethylene than other cyclanes (except cyclobutane). Most of the reagents that bring about the opening of the double bond also effect fission of the cyclopropane ring, though much less readily. Thus, we have :



Cyclopropane, however, does *not* react with cold permanganate[1] solution or with ozone (contrast ethylene).

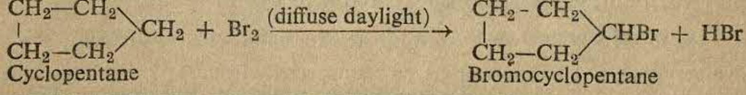
Cyclobutane ring is much less readily ruptured. Thus, the compound is not attacked by hydrogen iodide. When submitted to hydrogenation in the presence of nickel at 100°, there occurs no reaction. At higher temperatures (180°—200°) the ring is ruptured with the production of *n*-butane, $CH_3CH_2CH_2CH_3$.

Cyclopentane and higher members are quite stable towards the above reagents. Their behaviour is closely analogous to that of alkanes. Drastic treatment with certain reagents, however, may sometimes bring about ring fission. Thus, cyclohexane, when heated with concentrated nitric acid or treated with potassium permanganate, gets oxidized to adipic acid with rupture of the ring :—



$$\underset{\text{Cyclohexane}}{\begin{array}{l} CH_2-CH_2-CH_2 \\ | \qquad\qquad\quad | \\ CH_2-CH_2-CH_2 \end{array}} + 5O \rightarrow \underset{\text{Adipic acid}}{\begin{array}{l} CH_2-CH_2-COOH \\ | \\ CH_2-CH_2-COOH \end{array}} + H_2O$$

(4) **Substitution in Cyclane Rings.** As already stated, cyclopentane and higher members closely resemble the saturated hydrocarbons of the methane series, and are hardly distinguishable from them in general behaviour. They do not react with chlorine or bromine in the dark, but in the presence of light, *substitution* occurs with evolution of HCl or HBr ; *e.g.*,



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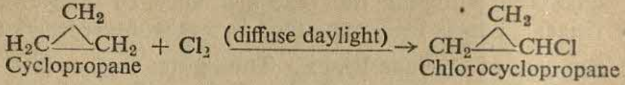
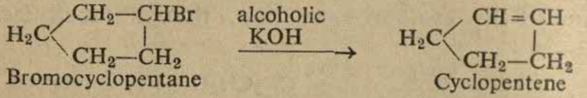
[1] Baeyer's permanganate test for the presence of double bond is therefore specific also in the presence of cyclopropane derivatives.

Chlorine in diffuse daylight substitutes even in the cyclopropane ring, producing chlorocyclopropane,

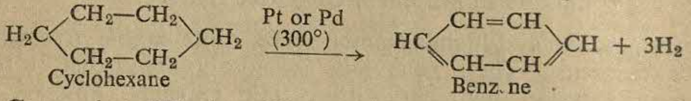


Chlorine or bromine attached to the carbon of a cyclane ring is as reactive as that in an alkyl halide, and may be replaced by OH, NH_2, etc., groups by means of the usual reagents. When treated with *alcoholic* potassium hydroxide, bromocyclanes lose HBr with the production of **cyclo-alkenes** ; *e.g.*,

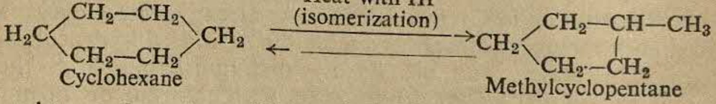


The cycloalkenes closely resemble olefines, and exhibit similar behaviour.

(5) **Aromatization of Cyclohexane Ring.** The cyclohexane ring and the benzene ring are interconvertible under suitable conditions. In section 3 of this chapter we saw that aromatic compounds constitute an important source of cycloparaffins and their derivatives. The reverse process of aromatization of the cyclohexane ring also occurs, and is utilized in the preparation of certain aromatic compounds from terpenes, etc. The simplest case of aromatization is that of the conversion of cyclohexane itself into benzene, which can be carried out at 300° in the presence of palladium or platinum :—



(6) **Conversion of Cyclane Rings.** An interesting phenomenon in the chemistry of alicyclic compounds is the contraction or expansion of the cyclane rings, which may occur during certain chemical reactions. Thus, when cyclohexane is heated with hydriodic acid at 200° to 300°, or boiled with an aqueous solution of aluminium chloride, partial conversion into methylcyclopentane occurs :—



There exists a **dynamic equilibrium** between the two hydrocarbons, which could be reached from either end. Methylcyclopentane, by the same treatment, is partially converted into cyclohexane.

5. Individual Cyclanes.—

Cyclopropane, C_3H_6 is now prepared commercially from 1, 3-dichloropropane in 80 per cent yield by a modification of Freund's method, developed by Hass in 1936. 1, 3-Dichloropropane (a product of chlorination of propane from natural gas) is treated with zinc dust and aqueous alcohol containing sodium iodide as catalyst and also sodium carbonate to regenerate sodium iodide from zinc iodide formed in the reaction.

Cyclopropane is the **most potent anesthetic gas** that produces insensibility to pain without unconsciousness.

Cyclobutane, C_4H_8, is prepared by the hydrogenation of cyclobutene in the presence of nickel. It is a liquid in winter (b.p. 12°), but changes to gas in the hot weather. Its chemical behaviour, which has already been described in the preceding section, is intermediate between cyclopropane and cyclopentane.

Cyclopentane, C_5H_{10}, occurs in Caucassian and American petroleums. Synthetically, it may be obtained from 1,5-dibromopentane by Freund's method. It is a mobile liquid (b.p. 49°). The cyclopentane ring is quite stable under ordinary conditions, though it does undergo fission on hydrogenation at 300° and on oxidation with nitric acid.

Cyclohexane, C_6H_{12}, occurs in Caucassian petroleum. It is commercially prepared from benzene of coal-tar by hydrogenation, and is **used as a solvent.**

The chemical behaviour of cyclohexane is similar to that of cyclopentane, except that it can be readily dehydrogenated to benzene (aromatization). When oxidized with potassium permanganate (or nitric acid) it gives adipic acid. Fuming sulphuric acid brings about aromatization followed by sulphonation, resulting in the production of benzenesulphonic acid, $C_6H_5SO_3H$.

According to **Sachse-Mohr theory,** cyclohexane occurs in a boat- and a chair-form (p. 71). From Raman and infra-red spectra and other physical evidence, it is concluded that at the ordinary temperatures the hydrocarbon exists mainly in the chair form. On vaporization, the chair form partially passes into the boat form.

QUESTIONS

1. Describe briefly Baeyer's Strain theory as applied to cycloparaffins and its limitations. How do you explain the existence of large-size rings containing 10 or more carbon atoms ?

2. What are cycloparaffins and how would you correlate their stability with molecular structure ? Give the general methods of preparation of these compounds. (*Punjab, B.Sc. 1949, 1953, 1954*)

3. Give a general account of the chemistry of polymethylenes. Show how Baeyer's Strain theory accounts for the relative stability of polymethylene rings. (*Bombay, B.Sc. 1953*)

4. Describe different methods by which cycloparaffins have been synthesized. (*Dacca, B.Sc., Hons., 1937; Annamalai, 1941*)

5. Discuss the chemistry of the cyclo-paraffins, bringing out the change in chemical properties with a change in the number of carbon atoms in the ring. What do you know of strainless rings ? (*Bombay, B.Sc., 1941*)

6. Give a general account of the chemistry of polymethylenes. Show how Baeyer's strain theory accounts for the relative stability of such things. How has the existence of large carbon rings been accounted for ? (*Bombay, B.Sc., 1952*)

7. Describe the different methods of preparing polymethylenes. What is Baeyer's Strain theory ? (*Bombay, B.Sc., 1957*)

8. Give an account of Baeyer's strain theory and subsequent modifications. How are large-ring cycloparaffins synthesised from open-chain compounds ? (*Gujarat, B.Sc., 1958*)

9. State briefly Baeyer's strain theory as applied to cyclic compounds, and describe the lines on which the theory has been extended and developed. (*B.Sc., London, 1931*)

10. Give a general account of the Chemistry of polymethylenes. Show how Baeyer's Strain Theory accounts for the relative stability of such rings.
(*Bombay, B.Sc., 1953*)

11. What do you know about the polymethylenes ? What is Baeyer's strain theory ?
(*Dacca, B.Sc., Hons. 1933*)

12. How are the cycloparaffins prepared ? Discuss their stability in the light of Baeyer's Strain Theory and its later developments.
(*Jammu & Kashmir, B Sc., 1960*)

13. Describe general methods of preparation of cycloparaffins. Write a short note on their order of stability.
(*Madras, B.Sc., 1960*)

14. How can cyclo-alkanes be obtained ? How far does the stability of such ring systems depend on the number of carbon atoms present in the ring ?
(*Punjab, B.Sc., 1962*)

CHAPTER THIRTY-SIX

INTRODUCTION TO AROMATIC SERIES

1. Aromatic Compounds.—Aromatic compounds are derived from the hydrocarbon *benzene*, C_6H_6, just as the aliphatic compounds are derived from methane. Certain of the substances derived from benzene were originally obtained from aromatic resins and oils. While the actual constitution of these compounds was then unknown, they all were found to possess a pleasant, aromatic odour; hence they were grouped together as *aromatic compounds*. The term "aromatic" is now reserved for benzene derivatives and, in general, for all carbocyclic compounds which are similar in character to benzene.

2. Destructive Distillation of Coal.—The main source of the aromatic compounds is the tar obtained as a by-product in the destructive distillation of coal at temperatures above 1,000°C. This is carried out either for the manufacture of coal-gas or of coke required for the metallurgy of iron and other metals.

The plant employed in the manufacture of coal-gas is shown in Fig. 1. Gas-coal (*i.e.*, coal rich in hydrogen and yielding a high proportion of gas) is heated in fire-clay retorts (shown on the left-hand side of the figure) heated by a coke fire. The volatile products bubble through water in a hydraulic main, where most of the tar gets condensed. The gas then passes through condensers, or a series of air-cooled pipes, where the rest of the tar gets condensed. Next, the gas passes upwards through a scrubbing tower, packed with loose coke, down which water is sprayed. Here, most of the ammonia and some of the hydrogen sulphide present in the gas is removed. It is then led into a purifier, containing trays filled with moist ferric hedroxide or lime, where the rest of the hydrogen sulphide is absorbed. The purified gas is collected over water in gas-holders, and delivered under pressure into distributing mains.

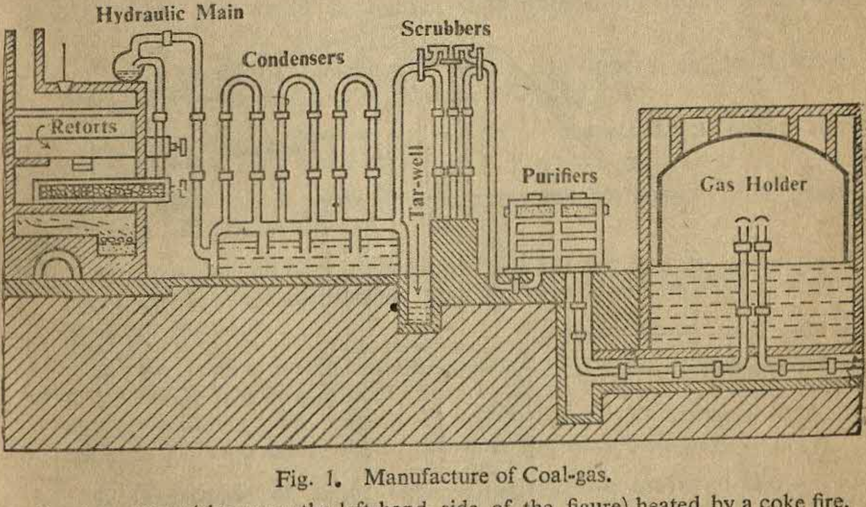


Fig. 1. Manufacture of Coal-gas.

3. Fractional Distillation of Coal-tar.—Coal-tar is a thick, black liquid with a characteristic acrid odour. It is an extremely complex mixture of naturally occurring neutral, basic and acidic substances. The first are chiefly hydrocarbons of the aromatic series. From 5 to 10 per cent of the tar consists of naphthalene, and from 1 to 1·5 per cent of a mixture of benzene and toluene. Basic constituents, which are present only in small proportions, include pyridine, quinoline, and their homologues. The principal acidic constituent of tar is phenol or carbolic acid.

Separation of various constituents of tar is effected by (*i*) fractional distillation, and (*ii*) chemical treatment.

The tar received from the gas works is run into a tank, and allowed to stand, until the ammoniacal liquor mixed with it has separated by gravity. The separation is facilitated, especially in the cold weather, by a steam coil laid in the tank. If the ammoniacal liquor is not completely removed before distillation, it would cause frothing in the still.

The plant employed for the distillation of coal-tar is shown in Fig. 2. The tar-still is made of iron and has a capacity of 20 to 30 tons. The top consists of a cast iron dome provided with (*i*) a manhole, *M*, (*ii*) an inlet pipe, *P*, for tar, (*iii*) a broad, curved vapour pipe, *V*, (*iv*) a thermometer tube, *T*, and (*v*) a safety valve, *S*. The bottom of the still is concave, and rises to a considerable height. This ensures the distribution of heat into the interior of the mass of

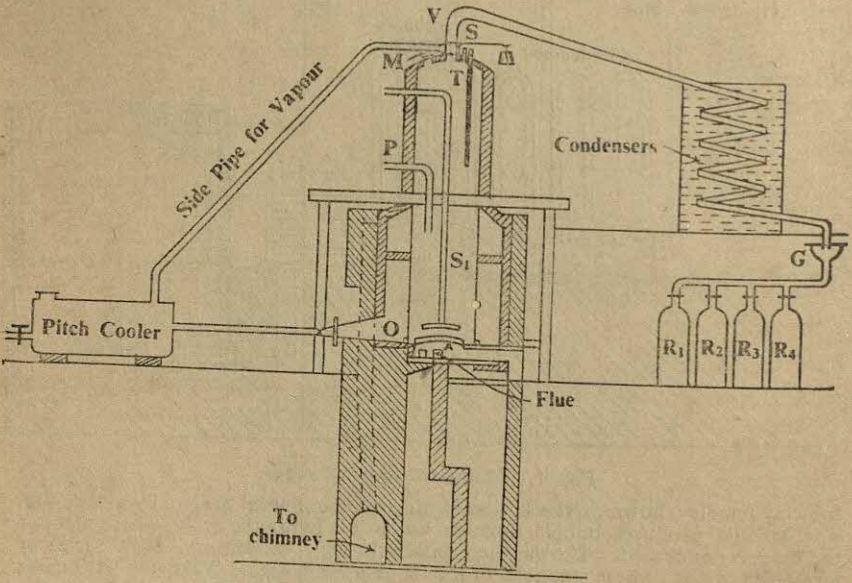


Fig. 2. Fractional Distillation of Coal-tar.

tar, and further, since the outlet pipe, *O*, is placed at the lowest point, it is also helpful in emptying the still at the end of the operation. The bottom is usually protected from direct contact with the flames by a brick-work arch, *A*. The still is provided with a steam-coil S_1, through which superheated steam is blown towards the end of the operation to facilitate the distillation of the heavy oils. The still is set in a furnace so that the flames play under the bottom and about halfway up the height, through side-flues in the brick-setting.

The condenser consists of an iron worm placed in a tank. The latter is provided with a steam pipe to warm the water if necessary. The various fractions are collected in separate receivers, the process being checked by occasionally noting the specific gravity of the distillate in a suitable outlet vessel, *G*.

The tar is run into the still while the latter is still hot from a previous operation. When the charging is about one-half completed, the heating is started and the fire is carefully controlled till the cracking noise in the still has ceased. This is an indication that the water has all been carried over. The fire can now be 'pushed' so that the distillate runs at the rate of 4 to 6 gallons per minute. The distillate is usually collected in the following four fractions :—

(1) **Light oil**, which is lighter than water and distils between 80° and 170°.

(2) **Middle oil**, or **carbolic oil**, which has approximately the same density as water, and distils between 170° and 230°.

(3) **Heavy oil** or **creosote oil**, which is heavier than water, and distils between 230° and 270°.

(4) **Green oil** or **anthracene oil**, which is green in colour, and distils between 270° and 400°.

Towards the end of the operation superheated steam is admitted into the still to aid distillation, which is carried on until the distillate becomes resinous.

The fire is now drawn and the residue in the still, known as **pitch**, is run, while still hot[1] into the pitch cooler—a closed tank provided with a manhole. The latter is closed with a loosely fitting lid, which, while it acts as a safety valve, prevents free access of air.[2]

4. **Treatment of Light Oil.**—This fraction, on being allowed to stand, deposits a small quantity of *ammoniacal liquor*, which is drawn off. The oily layer which contains, in addition to *benzene hydrocarbons*, appreciable quantities of *pyridine bases* and *phenols*, is first agitated with dilute sulphuric acid in a lead-lined, cone-bottomed

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[1] The still must be emptied while the pitch is still sufficiently hot to drain out completely ; if any of it is left in the still, the heat of the brick work will convert it into coke, which sticks very firmly to the still bottom and prevents heating of the next charge.

[2] If a free access of air is permitted the hot pitch would catch fire.

tank. The acid layer is run off, and treated with lime, when the mixture of **pyridine bases** separates out as an oil. The latter, after redistillation, is employed in denaturing alcohol, and as a solvent for the purification of crude anthracene.

The light oil, freed from the basic substances, as given above, is now treated with sodium hydroxide solution, which removes phenols. After running off the alkaline liquid, the oil is agitated with about 5 per cent of concentrated sulphuric acid, the temperature being kept low. By this means *thiophene* and *olefines* are dissolved and more complex substances are charred. After running off the acid tar, the oil is washed with a little sodium hydroxide solution to remove sulphur dioxide, etc., and finally washed with water.

The neutral oil, thus obtained, is now redistillled, using a still provided with a rectifying column and cooler for fractional condensation (Fig. 3). The cooler consists of a number of chambers (*C*, *C*) surrounded by a water bath, which may be kept at any desired temperature. Here, the high-boiling components get condensed and flow back to the fractionating column, while the low boiling components pass on to the water-cooled worm condenser.

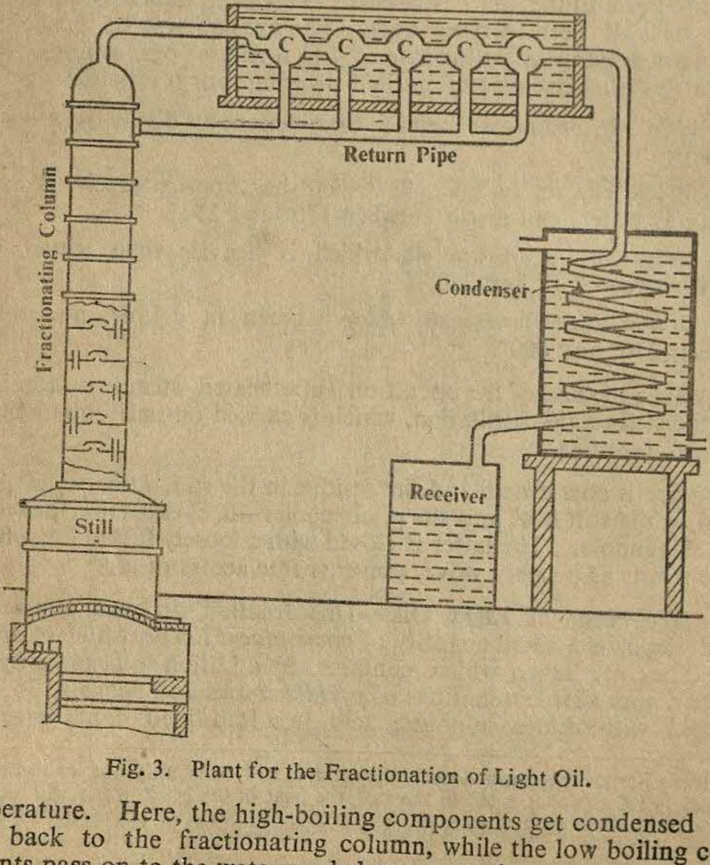

Fig. 3. Plant for the Fractionation of Light Oil.

In the fractionation of light oil the following fractions are collected in the first instance :—

(1) *90 per cent benzol*, up to 95°,

(2) *50 per cent benzol*, up to 125°,

(3) *Solvent naphtha*, up to 170°.

The residue in the still, which contains naphthalene and heavy oil, is added to the second fraction from the tar still.

The terms "90 per cent benzol" and "50 per cent benzol" do *not* indicate the benzene content, but refer to the proportions by volume of the fraction that distils up to 100°C. The two fractions consist of a mixture of benzene and toluene, the 90 per cent benzol containing about 70 per cent of benzene, and the 50 per cent benzol about 46 per cent of it. The two fractions are separated into pure benzene (*b.p.* 80°) and pure toluene (*b.p.*, 110°) by systematic refractionation. The residue, which consists of xylenes etc., is mixed with solvent naphtha.

The solvent naphtha consists mainly of xylenes and higher hydrocarbons, and is used as a solvent for resins and rubber.

5. **Treatment of Middle Oil.**—The *middle* or *carbolic oil*, consists mainly of **naphthalene** and phenols On allowing it to cool, most of the naphthalene crystallizes out, and is removed by centrifugation. The crystals are washed with hot water in centrifugals to remove most of the adhering oil. The crude product is then melted and treated, in lead-lined agitators, with sulphuric acid to remove phenols. The spent acid is completely run off, and the naphthalene is then washed with water, and finally with caustic soda solution. After running off the alkali solution completely the naphthalene is distilled. The "heads" and the "tails" of the distillate are both rejected, the former because they are discoloured by the washings of the condenser and the latter because they contain the oil. The portion thus rejected should not exceed 1 per cent of the distillate.

The oily mother liquor from which naphthalene has been removed is agitated at about 60° with a sufficient quantity of dilute sodium hydroxide solution, which dissolves out the phenols. The alkaline liquid containing sodium phenates is subjected to steam distillation to remove the hydrocarbon impurities, and is then treated with sulphuric acid or carbon dioxide to set free the phenols. The latter are then submitted to fractional distillation in column stills. Three fractions are collected; the first, collected at 180° to 183°, consists of crystallizable **phenol**, the second does not contain a sufficient quantity of phenol to crystallize, while the third one consists principally of **cresols.**

6. **Creosote Oil.**—The "heavy oil" or "creosote oil" is a greenish-yellow, fluorescent liquid, heavier than water. It contains phenols, cresols, naphthalene and other substances, but the constituents are

not usually separated. Creosote oil is chiefly employed for the preservation of timber.

7. **Treatment of Green Oil.** Green oil or anthracene oil contains anthracene, naphthalene, phenanthrene, and certain other solid hydrocarbons and also some liquid hydrocarbons (*e.g*, methylnaphthalene) of high boiling-point. The oil is run into shallow tanks and allowed to stand for one to two weeks, when the solid mass is filter-pressed, and the resulting cakes, containing about 15 per cent of anthracene are subjected to a pressure of 50,000 lb. or more between steam-heated plates of a filter press. This treatment increases the anthracene content to about 30 per cent. The product is now powdered and washed with pyridine bases mixed with solvent naphtha to dissolve out phenanthrene and other impurities. In this manner a product containing about 80 per cent of anthracene is obtained. This, on sublimation, or distillation in steam, yields the so-called 90 *per cent anthracene* of commerce, which is directly employed in the manufacture of dyes.

8. **Pitch.**—The pitch ordinarily obtained from the tar-still is what is termed the **hard-pitch.** To facilitate the removal of pitch from the still, and also to meet the demand for **soft-pitch**, it is often the practice to pump into the still creosote oil or "dead oils" from which anthracene, or naphthalene and phenols have been extracted. These mix with the hot pitch, yielding a product of any desired consistency, according to the amount of oil used. Pitch is much employed for making black paints, and varnishes for metal and wood work, for making tarred felt or paper, and as a binder in roof-making, and in preparing fuel *briquettes* from coal dust.

9. **Light Oil from Coke Oven Gas.**—Very large quantities of coal are converted into coke for use in metallurgy. The conditions under which coking is carried out are somewhat different from those employed in making coal-gas. The coal is heated at 1300° in **recovery ovens** made of fireclay. The evolved gases pass through condensers, tar and ammonia scrubbers, and then through oil-absorption towers in which creosote oil is sprayed from the top. The vapour of benzene, toluene, xylenes and naphthalene contained in the gases are dissolved out by the creosote oil and are recovered from it as **light oil** by steam-distillation.

The **coke-oven tar** also gives some light oil on distillation, but the major part is derived from the oil-scrubbing of coke-oven gas.

10. **Petroleum as a source of Aromatic Compounds.**—Nowadays, petroleum is being increasingly employed as a source of aromatic compounds. Most petroleums have been found to contain a wide variety of aromatics, and as many as fourteen have been isolated from the gasoline fraction of petroleum distillation. These include benzene, toluene, cumene and pseudocumene. The aromatic content of Borneo crude is about 40 per cent, and in the World War I the Borneo petroleum served as an important source of toluene, which

is a strategic material employed in the production of the high explosive T.N.T. The kerosene fraction of some petroleums has been found to contain alkylbenzenes, naphthalene and alpha- and beta- methylnaphthalenes and also certain other aromatics.

The **aromatization** of aliphatic compounds is a very important means of producing aromatics from aliphatic products obtained from petroleum. Benzene and toluene are now manufactured from *n*-hexane and *n*-heptane respectively (see page 143). A new catalytic process of aromatization of heavy naphthas, called **hydroforming**, was developed in 1941, and is mainly employed in the production of high-octane gasolines. The reaction is carried out in the presence of hydrogen, and the net effect is dehydrogenation and aromatization. The product is separated into three fractions. The first fraction is rich in benzene, the second in toluene and the third in xylenes. The middle fraction is mostly employed in the manufacture of explosives, the first one in blending motor petrols and the third one in blending aviation petrols on account of the very high octane rating (sec. 20, p. 184) that it possesses.

11. Coal-Tar Industry in India.—The main source of coal-tar in India is the coke ovens attached to iron and steel works. About 50,000 tons of crude coal-tar is treated every year by the coal-tar distillation units. The output figures for the main products are: Naphthalene, 600 tons; Phenol, 50 tons; Cresols, 100 tons; Benzene, 200,000 gallons; Toluene, 50,000 gallons and Solvent naphtha, 10,000 gallons.

Vigorous attempts are being made to develop the coal-tar industry so as to enable it to meet the growing need of the new dye-stuff industry in this country.

QUESTIONS

1. What are the commercial sources of aromatic compounds, and how are they isolated from them?

2. Describe precisely what happens when coal-tar is subjected to fractional distillation. How would you isolate benzene, toluene and phenol from the crude distillate in a state of approximate purity? (*Calcutta, B.Sc., 1934, 1938*)

3. Give a brief account of the products obtained by the destructive distillation of coal. How are the important components of coal-tar separated? (*Madras, B.Sc., 1940*)

4. What are the important components of coal tar and how are they separated? (*Allahabad, B.Sc., 1951*)

5. Write an account of petroleum as a source of aromatic compounds. Explain the terms "*aromatization*" and "*hydroforming.*"

6. How will you obtain benzene, in the pure state, from a mixture of benzene toluene, aniline, phenol and water? (*Rajasthan, B.Sc., 1956*)

7. Describe in detail what happens when coal-tar is subjected to fractional distillation. How would you isolate benzene, toluene, and phenol from the crude distillate in a state of purity? What impurity is usually present in coal-tar? How is it detected and removed? (*Aligarh, B.Sc., 1955*)

8. Describe the usefulness of coal-tar in the preparation of organic compounds of industrial importance. (*Gauhati, B.Sc., 1956*)

CHAPTER THIRTY-SEVEN

BENZENE

1. Occurrence of Benzene.—Benzene, C_6H_6, the parent hydrocarbon of the aromatic series, was first isolated by Faraday in 1825 from oil-gas. Its presence in coal-tar was discovered in 1845 by A.W. Hofmann.

2. Commercial Preparation of Benzene.—Benzene is now obtained from two important sources:

(1) **From Coal-Tar.** The "light oil" fraction of coal-tar, after being treated with sodium hydroxide and concentrated sulphuric acid, as described in section 4, chap. 36, p. 541 is submitted to refractionation through most efficient fractionating columns of modern design. By this means, benzene and toluene are obtained in a high degree of purity. The third fraction, consisting of isomeric xylenes, is not usually separated into its components, but is employed as solvent under the name **"solvent naphtha."**

(2) **From Coke Oven Gas.** The light oil derived from the oil scrubbing of coke-oven gas (chap. 36, sec. 9, p. 544) is nowadays one of the major sources of commercial benzene (and also toluene, naphthalene etc.).

(3) **From Petroleum.** The "hexane fraction" of petroleum distillation is passed over chromic oxide catalyst heated at 460°, when cyclization followed by aromatization of *n*-hexane occurs (*p.* 143). The product is submitted to fractionation to separate benzene from the unchanged hexane and cyclohexane.

3. Laboratory Preparation of Benzene :—

(1) **From "Benzol".** A sample of pure benzene may be obtained in the laboratory from the commercial "90 per cent benzol" as follows :

(*a*) The commercial product is subjected to repeated fractionation in a flask provided with an efficient fractionating column, the fraction boiling at 80° to 81° being collected separately.

(*b*) The fraction collected at 80° to 81° is cooled by means of a freezing mixture, when crystals of almost pure benzene separate out, the impurities being, for the most part, left in the mother liquor. The crystals are quickly filtered and pressed in the cold between layers of filter paper. They may be melted, and the process of cooling repeated, if necessary[1].

(*c*) The product will contain about half a per cent. of **thiophene**, a sulphur compound whose boiling and freezing points are remarkably near to those of benzene. To remove this impurity, the benzene is shaken for a long time with *cold* concentrated sulphuric acid, which sulphonates and dissolves out the thiophene, while benzene remains practically unaffected. The treatment with sulphuric acid is continued, until the product ceases to give a blue coloration with concentrated sulphuric acid containing a trace of isatin (**indophenine reaction**). It is then redistilled.

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[1] This is ascertained by distilling the product ; the boiling-point should remain constant at 80°.

(2) **From Sodium Benzoate.** A very convenient method of preparing benzene in the laboratory is by distilling a mixture of sodium benzoate with soda-lime :—

$$\underset{\text{Sodium benzoate}}{C_6H_5COONa} + NaOH \rightarrow \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

The distillate separates into a lighter layer (benzene) and a heavier layer (water). The former, after being separated, is dried with anhydrous calcium chloride and redistilled.

4. **Syntheses of Benzene.**—Benzene can be synthesized in a number of ways, which may be considered under two headings :—

(*a*) **From Derivatives of Benzene :**

(1) Distillation of sodium benzoate with soda-lime, described above.

(2) From phenol by distillation with zinc dust,

$$\underset{\text{Phenol}}{C_6H_5OH} + Zn \longrightarrow \underset{\text{Benzene}}{C_6H_6} + ZnO$$

(3) From benzenesulphonic acid by boiling with concentrated hydrochloric acid (hydrolysis) :

$$\underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} + HOH \longrightarrow \underset{\text{Benzene}}{C_6H_6} + H_2SO_4$$

(4) From aniline through the diazo reaction :

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{HCl} \underset{\text{Aniline hydrochloride}}{C_6H_5NH_3Cl} \xrightarrow{HNO_2} \underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl}$$

$$\xrightarrow{+2H} \underset{\text{Benzene}}{C_6H_6} + N_2 + HCl$$

The reduction of the diazonium salt to benzene is effected by warming with an alkaline solution of stannous chloride.

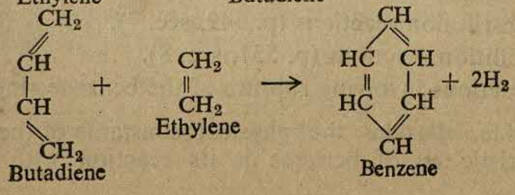
(*b*) **By Aromatization of Aliphatic and Alicyclic Compounds :—**

(1) **From Acetylene** (Berthelot's synthesis). When acetylene is passed through a red hot tube, it is converted into benzene (page 170, reaction 2). In the presence of nickel carbonyl catalyst, this conversion occurs at 60°—70° and a pressure of 15 atmospheres.

(2) **From Propane.** When propane is submitted to pyrolysis, it gives benzene through the following series of reactions :—

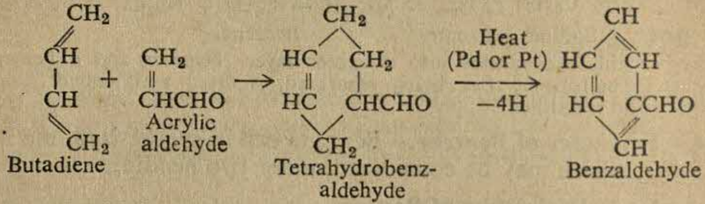
$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \longrightarrow \underset{\text{Ethylene}}{H_2C{=}CH_2} + \underset{\text{Methane}}{CH_4}$$

$$\underset{\text{Ethylene}}{2H_2C{=}CH_2} \longrightarrow \underset{\text{Butadiene}}{H_2C{=}CH{-}CH{=}CH_2} + H_2$$



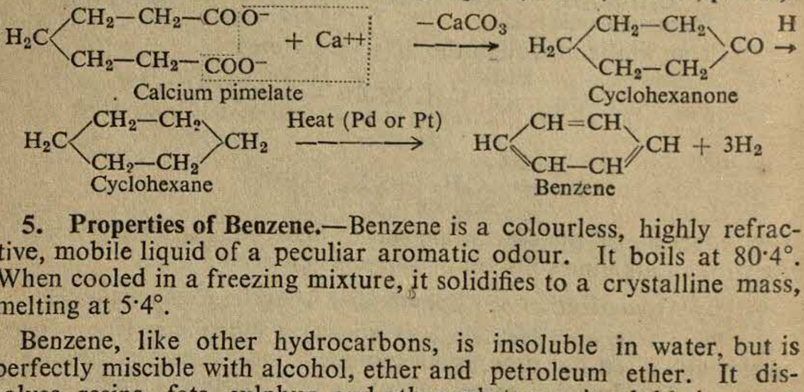
(3) **From Hexane.** (See p. 143)

(4) **Diels-Alder Reaction.** 1,3-Butadiene when heated with acrylic aldehyde undergoes Diels-Alder reaction (chap. 35, sec. 3, reaction 5, p. 533) to give tetrahydrobenzaldehyde. This, when heated with palladium or platinum catalyst, gives benzaldehyde,



Benzaldehyde may be converted to benzene by oxidation to benzoic acid, followed by distillation of the sodium salt of the acid with soda-lime.

(5) **From Pimelic Acid (Willstatter's Synthesis).** When calcium salt of pimelic acid is submitted to dry distillation, we get cyclohexanone, which when submitted to Clemmensen reduction (p. 275), gives cyclohexane. The latter when heated with palladium or platinum catalyst gets aromatized to benzene (chap. 35, sec. 4, reac. 5, p. 536).



5. Properties of Benzene.—Benzene is a colourless, highly refractive, mobile liquid of a peculiar aromatic odour. It boils at 80·4°. When cooled in a freezing mixture, it solidifies to a crystalline mass, melting at 5·4°.

Benzene, like other hydrocarbons, is insoluble in water, but is perfectly miscible with alcohol, ether and petroleum ether. It dissolves resins, fats, sulphur, and other substances insoluble in water, and, on this account, is extensively employed as a solvent.

Benzene, being as rich in carbon as acetylene, burns with a luminous smoky flame.

In **chemical reactions,** benzene differs entirely from the aliphatic hydrocarbons. Its reactions may be divided into three distinct groups :—

(*i*) Substitution reactions (p. 549, sec. 7).

(*ii*) Addition reactions (p. 551, sec. 8).

(*iii*) Reactions involving rupture of the benzene ring (p. 552, sec. 9).

Detection. Besides the physical constants of the hydrocarbon, a characteristic test of benzene is its reaction with nickel cyanide.

An ammoniacal solution of the substance yields with benzene a white, violet-tinted, crystalline compound of the formula, $Ni(CN)_2.NH_3.C_6H_6$.

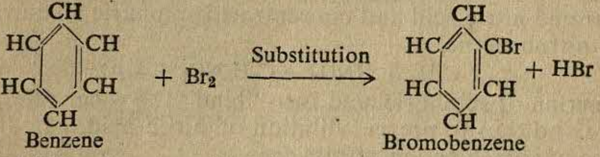
Uses. (1) The principal use of benzene is in the manufacture of nitrobenzene and other derivatives.

(2) It is employed as a solvent for resins, fats, etc.

(3) It is also used for dry-cleaning of woollen clothes.

6. Aromatic Character of Benzene.—The fundamental fact about the chemistry of benzene and its derivatives is the *"aromatic nature"* or **"aromaticity"** of the benzene ring. This refers in the first place to the peculiar structure of the benzene nucleus, which is a **cyclic and stable system of conjugated double bonds** with exceptionally great tendency to preserve its integrity during chemical reaction. It also refers to **certain distinctive characters** associated with this structure :—

The tendency of benzene and its derivatives to maintain the **benzenoid structure** is so great that, despite the presence in the ring of three double bonds, the characteristic reactions of benzene are *substitutions*[1] rather than additions. Thus, when treated with bromine, benzene gives bromobenzene, which still possesses the characteristic benzenoid nucleus :—



Similarly, with other reagents (see next section), benzene yields *substitution* products, which themselves possess the benzenoid structure and the characteristic aromatic behaviour.

Another point to notice in this connection is that the chemical behaviour of aromatic compounds having substituents in *direct union* with the benzene nucleus offers a striking contrast to that of the corresponding alkyl derivatives. Thus, phenols, unlike aliphatic alcohols, possess a marked acidic character. The aromatic halogen derivatives, with the halogen directly attached to the benzene nucleus, differ from aliphatic halogen compounds in exhibiting an almost entire lack of reactivity. Again, the amino-derivatives having the NH_2 group in direct union with the benzene nucleus react with nitrous acid *in the cold* in a unique manner, giving an important class of compounds, called the "diazonium salts", which have no counterpart among the aliphatic compounds.

7. Substitution Reactions of Benzene.—The reactions involving direct introduction of substituent groups in the benzene nucleus are called **aromatic substitutions.** They are :—

(1) **Aromatic Halogenation.** The reaction between a halogen and

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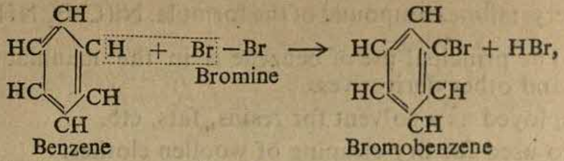
[1] As is well known, ethylene and other double bond compounds have great preference for *addition* reactions.

the benzene nucleus, *e.g.*,



occurs in the presence of such **aromatic halogenation catalysts** as ferric halides, aluminium halides, or iodine. The most common method is to use some iron filings, which change to a ferric halide in the reaction mixture.

While chlorination and bromination proceed smoothly, iodination, being a reversible process,

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI,$$

is generally carried out in the presence of an oxidizing agent (*e.g.*, nitric acid), which oxidizes hydrogen iodide, to iodine, and thus enables the forward reaction to proceed to a considerable extent. Thus iodobenzene may be obtained in 86% yield by the action of iodine on benzene in the presence of nitric acid.

(2) **Aromatic Nitration.** When benzene is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid at about 50°, it gives nitrobenzene,

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

The function of sulphuric acid is to "bind" the water produced in the reaction and thus to prevent dilution of nitric acid. It also diminishes the oxidizing action of nitric acid.

At a higher temperature (90°—100°C), 1,3- or *meta*-dinitrobenzene is produced.

(3) **Aromatic Sulphonation.** The sulphonation of benzene is carried out by heating the hydrocarbon with concentrated sulphuric acid. The reaction,

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 \rightleftharpoons \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} + H_2O,$$

is *reversible*, and a state of equilibrium is set up when the concentration of the acid has reached a certain value depending on the temperature.

In order to shift the equilibrium to the right, water must be removed from the reaction mixture by suitable means (*e.g.*, by carrying out the sulphonation under reduced pressure, by the addition of sulphur trioxide, or by passing an inert gas through the reaction mixture to carry off the water vapour).

(4) **Friedel-Crafts Reaction.** The French chemist Friedel and his American collaborator Crafts discovered in 1877 that pure anhydrous aluminium chloride is a very effective catalyst for the alkylation of aromatic hydrocarbons. Later, the reaction was found to be useful in preparing ketones and other compounds. The following are the more **important applications** of the Friedel-Crafts synthesis.

(*i*) *Synthesis of Aromatic Hydrocarbons.*—

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Ethyl chloride}}{ClC_2H_5} \xrightarrow{AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} + HCl$$

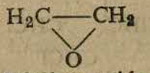
$$C_6H_5H + \underset{\text{Benzyl chloride}}{ClCH_2C_6H_5} \rightarrow \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + HCl$$

(*ii*) *Synthesis of Aromatic Ketones.*—

$$C_6H_5H + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

$$C_6H_5H + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \rightarrow \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$$

(*iii*) *Synthesis of Aromatic Alcohols.*—



$$C_6H_6 + H_2C\text{—}CH_2 \xrightarrow{AlCl_3} \underset{\beta\text{-Phenylethyl alcohol}}{C_6H_5CH_2CH_2OH}$$

Ethylene oxide

(*iv*) *Synthesis of Aromatic Aldehydes.*—

$$C_6H_6 + \underbrace{CO + HCl}_{\text{Formyl chloride}} \xrightarrow{AlCl_3} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

(*v*) *Synthesis of Acid chlorides.*—

$$C_6H_6 + \underset{\text{Carbonyl chloride}}{ClCOCl} \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

(5) **Mercuration.** An important and characteristic reaction of benzene and other aromatic compounds is that of *mercuration*, in which various **mercuri-acid groups** may be introduced in the aromatic ring. The compound to be mercurated is heated with mercuric salts; *e.g.*,

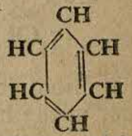
$$C_6H_6 + \underset{\substack{\text{Mercuric acetate}\\\text{(alcoholic solution)}}}{(CH_3COO)_2Hg} \rightarrow \underset{\substack{\text{Acetoxymercuribenzene}\\\text{(Phenylmercuric acetate)}}}{C_6H_5\text{—}HgOOCCH_3} + CH_3COOH$$

Mercuration with salts of strong mineral acids, *e.g.*,

$$C_6H_6 + HgCl_2 \rightarrow C_6H_5\text{—}HgCl + HCl,$$

$$C_6H_6 + Hg(NO_3)_2 \rightarrow C_6H_5\text{—}HgNO_3 + HNO_3,$$

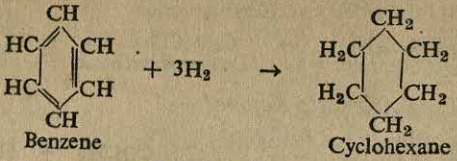
involves a complication, as the resulting mercuric compound is decomposed by the acid. In such a case, the reaction is carried out in the presence of mercuric oxide, to remove the mineral acid produced, and a suitable dehydrating agent, to eliminate water.



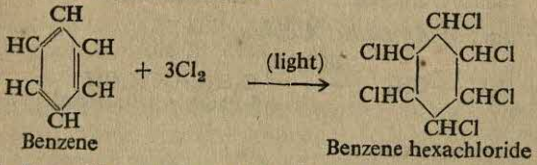
Benzene (1,3,5-cyclohexatriene)

8. Addition Reactions of Benzene.—The Kekule formula represents benzene as **cyclohexatriene-1,3,5** (see margin). This is in full agreement with the chemical behaviour of benzene as a triene under suitable conditions, *the benzene ring passing into the cyclohexane ring.*

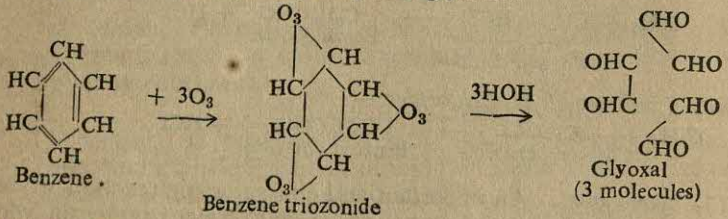
(1) **Catalytic Hydrogenation.** When submitted to hydrogenation in the presence of Raney nickel, platinum or palladium, benzene gives cyclohexane :—



(2) **Catalytic Chlorination or Bromination.** Benzene in the presence of light and absence of oxygen, adds on chlorine and bromine, yielding benzene hexachloride or hexabromide :



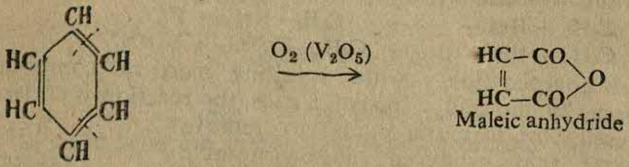
(3) **Ozonide Formation and Ozonolysis.** With ozone, benzene gives a **triozonide**, which when hydrolysed yields glyoxal :



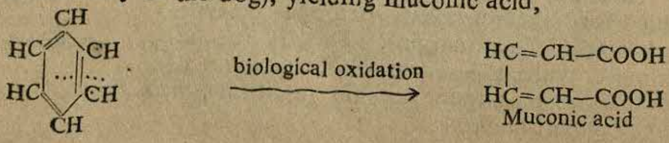
9. Ring Fission of Benzene.—Oxidation often results in the rupture of the benzene ring. The more important examples are :—

(1) Ozonolysis of benzene to glyoxal (3 molecules) just described.

(2) Vapour-phase oxidation of benzene with vanadium pentoxide as the catalyst, resulting in the formation of maleic anhydride,



(3) Biological oxidation of benzene (which has been found to occur in the body of the dog), yielding muconic acid,



10. Constitution of Benzene.—

(1) Open-chain formula untenable—

The molecular formula of benzene, as found by combustion and molecular weight determination, is C_6H_6. The low proportion of hydrogen to carbon indicates that benzene, like ethylene and acetylene, should possess an unsaturated nature, but most of its properties are in direct opposition to this assumption. Thus, whereas unsaturated compounds readily form addition-products with chlorine and bromine, are easily attacked by oxidizing agents, and at once react with Baeyer's reagent, benzene does not possess these properties. It must, therefore, be concluded that the molecular structure of benzene is entirely different from that of the unsaturated compounds, and that the carbon atoms in the benzene molecule must be linked together in a pattern not met with among the aliphatic or open-chain compounds.

(2) Kekule's Closed-chain Formula (1865)—

The formula of benzene that is now universally accepted was proposed by the German chemist Kekule in 1865, as the result of exceptionally brilliant intuition. Kekule was guided by the following two facts already established in connection with the chemistry of benzene derivatives :—

(1) *The monosubstitution products of benzene occur only in one form.*

(2) *The disubstitution products occur in three isomeric forms.*

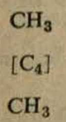
From (1) it follows that the six hydrogen atoms are *symmetrically* distributed within the molecule. For this to be true, the following two conditions must be satisfied :—

(*i*) The six hydrogen atoms must be *equally* distributed between a certain number of carbon atoms.

(*ii*) The hydrogen-bearing carbon atoms must themselves be symmetrically arranged within the molecule.

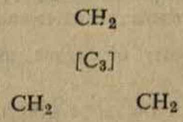
Hence there are but three structures possible for benzene :—

I.



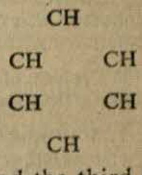
$$\begin{matrix} CH_3 \\ [C_4] \\ CH_3 \end{matrix}$$

II.



$$\begin{matrix} & CH_2 & \\ & [C_3] & \\ CH_2 & & CH_2 \end{matrix}$$

III.



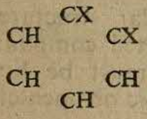
$$\begin{matrix} & CH & \\ CH & & CH \\ CH & & CH \\ & CH & \end{matrix}$$

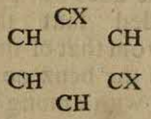
The first formula contains two, the second three, and the third six symmetrically arranged carbon atoms. The arrangement of the carbon atoms within the square brackets is immaterial, so long as it is symmetrical with respect to the hydrogen-bearing carbon atoms.

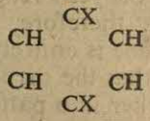
To decide which of the above formulae represents the benzene molecule, we must take into account the fact (2) given above, *viz.*, that the *disubstitution* products of benzene occur in three isomeric forms. Now, each of the formulae I and II can give rise to only *two* isomeric disubstitution products :

Formula I :	CH_2X $[C_4]$ CH_2X	CHX_2 $[C_4]$ CH_3
Formula II :	CHX $[C_3]$ $CH_2 \quad CHX$	CX_2 $[C_3]$ $CH_2 \quad CH_2$

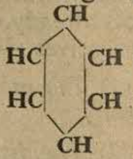
Hence, neither of these can represent the benzene molecule. The third formula, however, is capable of giving rise to three disubstitution products:







and, therefore, represents the benzene molecule. Thus we see that the molecule of benzene consists of six carbon atoms, each of which is symmetrically placed within the molecule and carries one hydrogen atom. The arrangement *cannot be represented by an open-chain formula*, since in that case the terminal and intermediate CH groups would not be equivalent, Kekule, therefore, came to the conclusion that *the molecule of benzene must consist of a closed chain of six carbon atoms, to each of which is linked one atom of hydrogen, as shown in the margin.*

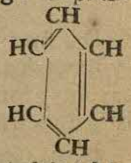


The cyclic formula of benzene is fully supported by numerous investigations of isomeric benzene derivatives. An evidence of independent nature is provided by **the X-ray crystallographic analysis of graphite.** The interesting compound **mellitic acid,** $C_6(COOH)_6$, has proved a link between graphite and benzene. It can be prepared, on the one hand, from known derivatives of benzene, and on the other, by the oxidation of graphite with nitric acid. X-ray analysis of graphite shows that its crystal lattice consists of a series of honeycombs of 6-membered carbon rings. This correlates benzene with graphite, and proves the 6-carbon ring structure of the hydrocarbon.

Another evidence in favour of the cyclic formula is the fact that a number of benzene derivatives have been converted into the corresponding compounds of the cyclohexane series. The most noteworthy case is the information of cyclohexane by catalytic hydrogenation of benzene (Sabatier and Senderens, 1901).

(3) **Problem of the fourth valency of carbon atoms of the benzene ring—the cyclohexatriene formula.—**

The simplest formula for benzene given above, though explaining the existence of one mono- and three disubstitution products of benzene, had a serious drawback. It represented the carbon atoms as possessing *three* covalencies only, which meant a contradiction of Kekule's theory of tetracovalency of carbon. Kekule met this difficulty by introducing three double bonds into the benzene ring in the alternate positions as shown in the margin.



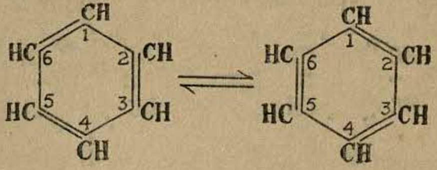
Kekule's 1,3,5-Cyclohexatriene formula for benzene

This newly proposed formula represents benzene as 1, 3, 5-**cyclohexatriene.** It is fully supported by the addition reactions of benzene described in sec. 8, particularly the formation of the triozonide and its decomposition by water to glyoxal It is also supported by the parachor determination of benzene and a large number of its derivatives.

The unusual stability of the benzene ring, in spite of there being three double bonds in it, is explained by the double bonds constituting a **closed chain conjugated system** with great tendency to preserve its integrity.

(4) **Kekule's Oscillation formula.—**

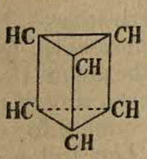
Ladenburg put forward a serious objection to the cyclohexatriene formula. The two *ortho*-positions in this formula are dissimilar. Hence, if we take the formula as correct, there should exist not three but *four* disubstitution products : *viz.*, 1 : 2, 1 : 3, 1 : 4, and 1 : 6. To meet this objection, Kekule suggested a **dynamic formula** or **oscillation formula** in which the fourth valency is assumed to be in a state of rapid oscillation between the two extreme positions as shown in the following scheme :



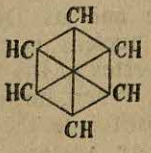
The above assumption does away with the distinction between positions 1 : 2 and 1 : 6. Thus the occurrence of the disubstitution products in only three forms is justified.

(5) **Other Formulae.—**

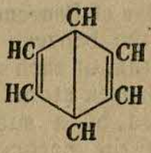
Other proposals for the saturation of the fourth carbon valency in the benzene formula were made from time to time. Ladenburg (1869) proposed the *prism* formula, Claus (1867) and Dewar (1887) suggested the existence of diagonal or *para* bonds while Armstrong in England (1887) and Baeyer in Germany (1887) put forward the concept of the *centric* formula in which the fourth valency of each of the six carbon atoms is represented as being directed towards the centre of the ring.



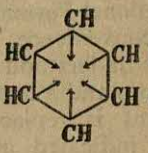
Ladenburg (1869)



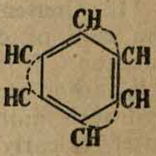
Claus (1867)



Dewar (1867)



Armstrong-Baeyer (1887)



Thiele (1899)

Thiele (1899) extended his theory of partial valency (page 73, sec. 12) to the benzene ring, and concluded that the three double bonds in Kekule's benzene formula constitute a *closed* conjugated system with no "ends" or points of special reactivity. This, according to Thiele, explains the failure of benzene to readily react with the usual double-bond reagents.

All the above formulae, however, have been rejected on account of stereochemical objections and physical evidence against them.

(6) Evidence of Physical Methods.—

The X-ray and electron-diffraction methods have fully established the correctness of Kekule's formula to the exclusion of all others.

They have, moreover, supplied the following additional facts about the benzene nucleus:—

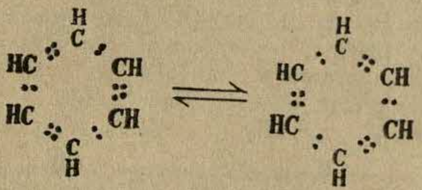
(*i*) The six carbon and the six hydrogen atoms of the benzene ring lie in a plane.

(*ii*) The distance between every pair of adjacent or *ortho* carbon atoms is the same (1·40 Angstrom).

(*iii*) All the six lines joining the carbon atoms of the benzene nucleus are of the same length, and thus form a *regular* hexagon.

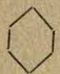
(7) Resonance in Benzene Ring.—

Kekule's oscillation formula, when expressed electronically, assumes the form,

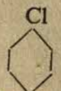


from which it is readily seen that the phenomenon here depicted is what we now call *resonance* (page 79, sec. 22). The two forms are perfectly equivalent and undistinguishable. Their interconversion requires a shift, not of the atomic centres, but of the electrons constituting adjoining bonds. Since each bond has the same hybrid character and rapidly alternates between a single and a double bond, the six bond lengths in benzene are equal. The unusual stability of the benzene ring, though partly due to its being a closed system of conjugated double bonds, is mainly the result of resonance.

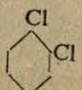
11. Conventional Formulae of Benzene and its Derivatives.—For the sake of convenience, the benzene nucleus is represented by a hexagon. It is understood that at each vertex of the hexagon there is a carbon atom and a hydrogen atom. When, however, any of the hydrogen atoms is replaced by a substituent, the symbol for the latter is clearly indicated at the particular vertex. The following examples illustrate the convention:—



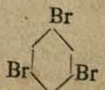
Benzene



Chloro-
benzene



1,2-Dichloro-
benzene



1,3,5-Tribromo-
benzene

QUESTIONS

1. What is benzene and what position does it occupy among organic compounds ? How would you prepare a *pure* sample of benzene in the laboratory ?

2. What are the important commercial sources of benzene and how is it obtained from them ?

3. Give two principal methods available for the introduction into the benzene nucleus of each of the following groups : Cl, CH_3, OH, and NO_2. How can each of these groups be eliminated from the nucleus, *i.e.*, replaced by hydrogen ?
(*Rajasthan, B.Sc.*)

4. Write a short note on Substitution in Benzene. (*Lucknow, B.Sc., 1961*)

5. Discuss the structure of Benzene. (*Gujarat, B.Sc., 1954*)

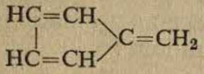
6. What evidence would you present in support of the ring structure of benzene ? How would you convert benzene into (*a*) toluene, (*b*) phenol, and (*c*) benzoic acid.
(*Osmania, B.Sc., 1956*)

7. How will you justify the assumption that the six hydrogen atoms in benzene are equivalent ? How would you show that toluene, aniline and phenols are derivatives of benzene ?
(*Nagpur, B.Sc., 1957*)

8. How is benzene obtained from coal-tar crudes ? What is the evidence for cyclic structure of benzene ? What experimental facts exclude the following formulae for benzene ?

(*a*) $HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$

(*b*) $H_2C{=}CH{-}C{\equiv}C{-}CH{-}CH_2$

(*c*) 

(*Rajputana, B.Sc., 1958*)

9. How do you arrive at the Kekule structure of benzene ? Discuss its merits and demerits.
(*Calcutta, B.Sc., 1960*)

10. Discuss the various structures that have been suggested for benzene. What is now the accepted structure and how does it explain fully its reactions ?
(*Allahabad, B.Sc., 1961*)

CHAPTER THIRTY-EIGHT

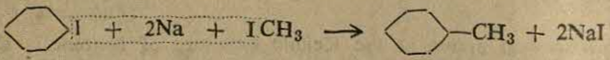
HOMOLOGUES OF BENZENE

1. Alkyl Benzenes.—The homologues of benzene are derived from benzene by the substitution of one or more atoms of hydrogen by alkyl groups The **general formula** of this homologous series is C_nH_{2n-6}. Toluene, or methylbenzene, $C_6H_5CH_3$, is the simplest of the alkyl derivatives of benzene. Many of the hydrocarbons of this series occur in coal-tar, but only benzene and toluene are isolated for use in industries.

The molecule of an alkylbenzene consists of two parts : the alkyl group, called the **side-chain,** and the benzene residue, called the **nucleus.**

2. General Methods of Formation.—

(1) **Wurtz-Fittig Synthesis.** This method discovered by Wurtz in 1855 for the building-up of carbon chains (page 137, reac. 3) was applied by Fittig (1864) to the synthesis of aromatic hydrocarbons with side chains. It consists in heating an aromatic halogen derivative with an alkyl halide and metallic sodium :



The presence of dry ether, ethyl acetate or benzene assists the reaction. The bromo- or iodo-derivatives react more readily than the corresponding chloro-derivatives.

(2) **Friedel-Crafts Hydrocarbon Synthesis.** This important synthesis was discovered by the French chemist Friedel and his American collaborator Crafts in 1877. It consists in the condensation of an *aromatic*[1] hydrocarbon with an *alkyl* chloride or bromide in the presence of **anhydrous aluminium chloride** as catalyst :

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Methyl chloride}}{ClCH_3} \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

The Friedel-Crafts hydrocarbon synthesis suffers from serious complications, which limit its usefulness to a considerable extent. One difficulty is that the alkylbenzene first formed readily undergoes further alkylation to give polysubstituted products. These subsequent reactions proceed more readily than the first one, and a mixture of products results. The separation of the desired product from this mixture involves considerable labour.

---

[1] The hydrocarbon must be *aromatic* and the halogen compound *aliphatic* (or a halogen derivative of an aromatic hydrocarbon with the halogen in the *aliphatic* side-chain. *e.g.*, $C_6H_5CH_2Cl$). Thus, toluene cannot be synthesized to any appreciable extent by the interaction of methane and chlorobenzene.

Another complication is that aluminium chloride may cause rearrangement of alkyl halides. Thus, *n*-propyl bromide reacts with benzene to give isopropylbenzene as the main product :

$$C_6H_6 + BrCH_2CH_2CH_3 \xrightarrow{AlCl_3} C_6H_5CH(CH_3)_2 + HBr$$

Similarly, other *primary* alkyl halides often give derivatives of *secondary* or *tertiary* alkyl halides, especially if the reaction is not carried out in the cold.

In spite of the above difficulties, the Friedel-Crafts method has proved very useful for the synthesis of aromatic hydrocarbons. Besides, aluminium chloride, which is the most active catalyst, **other catalysts of milder activity** have been found to be useful in moderating the reaction. The following catalysts, arranged in the order of activity, are suitable for various purposes.

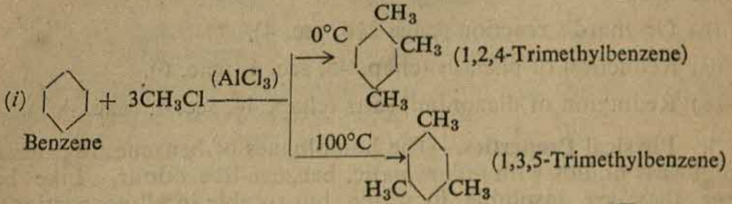
(*i*) *Anhydrous Inorganic Halides :*

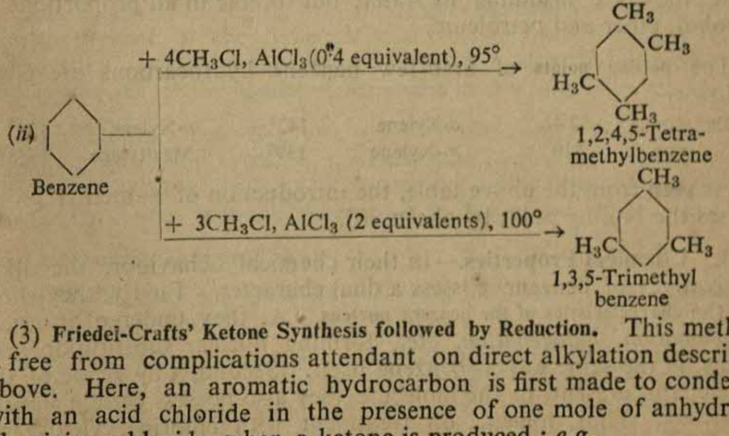
$$AlCl_3 > FeCl_3 > SnCl_4 > BF_3$$

(*ii*) *Inorganic Acids :*

$$HF > H_2SO_4 > P_2O_5 > H_3PO_4$$

The careful selection of the catalyst, the amount of the catalyst used and the regulation of temperature are important factors, especially in polysubstitutions. Comparatively **milder conditions have the ortho-para orientating influence** on the entering groups, while **more vigorous conditions cause meta orientation.** The following are illustrative examples :—





(*ii*)
Benzene
+ 4CH₃Cl, AlCl₃(0·4 equivalent), 95°
CH₃
CH₃
H₃C
CH₃
1,2,4,5-Tetra-methylbenzene
+ 3CH₃Cl, AlCl₃ (2 equivalents), 100°
CH₃
H₃C
CH₃
1,3,5-Trimethyl benzene

(3) **Friedel-Crafts' Ketone Synthesis followed by Reduction.** This method is free from complications attendant on direct alkylation described above. Here, an aromatic hydrocarbon is first made to condense with an acid chloride in the presence of one mole of anhydrous aluminium chloride, when a ketone is produced ; *e.g.*,

$$C_6H_5H + ClCOCH_3 \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

The resulting ketone is then heated with amalgamated zinc and concentrated hydrochloric acid (**Clemmensen reduction**), when an alkylbenzene is produced :—

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 4H \rightarrow \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} + H_2O$$

(4) **From Aromatic Acids.** When an aromatic acid or its calcium salt is heated with soda-lime, the carboxyl group is removed and a benzene hydrocarbon results :

$$\underset{\text{Toluic acid}}{C_6H_5(CH_3)COOH} + 2NaOH \longrightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + Na_2CO_3$$

(5) **From Aromatic Sulphonic Acids.** An aromatic sulphonic acid, when heated strongly with concentrated hydrochloric acid in a sealed tube, is hydrolysed to give the corresponding hydrocarbon :

$$\begin{array}{l} C_6H_4(CH_3)SO_2OH \\ \quad + H\,OH \end{array} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Sulphuric acid}}{SO_2(OH)_2}$$

The reaction is of importance for the **separation of a mixture** of hydrocarbons. Thus, if one hydrocarbon can be sulphonated under certain conditions and the other not, the latter can be readily extracted from the reaction mixture, and the former is then recovered from the residual sulphonic derivative by the above reaction.

The following reactions are also available, though they are not much used :

(6) Grignard's reaction (page 216, sec. 4).

(7) Reduction of phenols (chap. 45, sec. 4, reac. 6).

(8) Reduction of diazonium salts (chap. 44, sec. 4, reac. A,1).

3. Physical Properties.—The homologues of benzene are generally colourless liquids with an aromatic, benzene-like odour. Like benzene they are insoluble in water, but soluble in all proportions in alcohol, ether and petroleum.

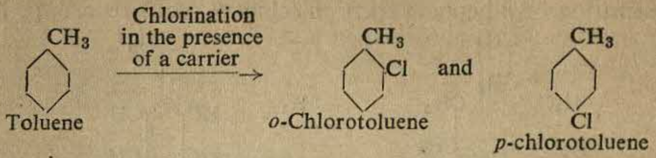
The **boiling points** of first few benzene hydrocarbons are given below :—

Benzene	80·4°	*o*-Xylene	142°	*p*-Xylene	138°
Toluene	110°	*m*-Xylene	139°	Mesitylene	165°

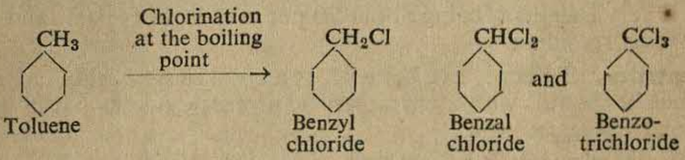
As seen from the above table, the introduction of a methyl group raises the boiling point by about 30°.

4. Chemical Properties.—In their chemical behaviour, the alkyl derivatives of benzene possess a dual character. Firstly, they show all the **characteristics of the benzene nucleus**, *i.e.*, they undergo *nitration*, *sulphonation*, *halogenation*, *etc.*, forming nuclear substitution products, in the same way as benzene itself. Secondly, by virtue of the side-chain present in the molecule, they also possess certain **aliphatic characters.** Thus, toluene, on treatment with chlorine, yields two kinds of products. When chlorine is passed into cold toluene in the presence of a halogen carrier (iron filings, aluminium powder, iodine, etc.), substitution occurs in the nucleus, and a mixture of *o*- and *p*-

chlorotoluenes is produced :



If, on the other hand, chlorine is passed into *boiling* toluene, preferably in direct sunlight, substitution occurs in the side-chain, the three hydrogen atoms of the methyl group being successively replaced by chlorine atoms (compare methane) :



A characteristic property of alkylbenzenes is their **behaviour on oxidation.** When treated with dilute nitric acid, chromic acid or potassium permanganate, the side-chain, no matter how long, is oxidized to a carboxyl group ; *e.g.*,

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

$$\underset{\text{Ethyl benzene}}{C_6H_5CH_2CH_3} + 6O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + CO_2 + 2H_2O$$

If the hydrocarbon contains two or more side-chains, *each* one of these is oxidized to a carboxyl group ; *e.g.*,

$$\underset{o\text{-Xylene}}{C_6H_4(CH_3)_2} + 6O \rightarrow \underset{\text{Phthalic acid}}{C_6H_4(COOH)_2} + 2H_2O$$

The reaction, therefore, may be used **to determine the number of side-chains** present in the molecule of a benzene homologue, by finding the basicity of the resulting acid. It may also be employed for **determining the relative position of side-chains** in the ring.

5. Toluene, *Methylbenzene*, or *Phenylmethane*, $C_6H_5CH_3$.—This hydrocarbon is present in coal-tar and in coke-oven gas. It also occurs among the products of destructive distillation of Tolu balsam, hence the name "toluene" given to it by Berzelius.

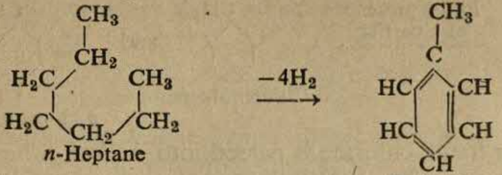
Commercial Preparation.—

(1) **From Coal-Tar.** The normal source of commercial toluene the coal-tar (chap. 36, sec. 2, page, 539).

(2) **From Coke Oven Gas.** Considerable quantities of toluene are now obtained from the "light oil" derived from the coke-oven gas (chap. 36, sec. 9,page 544).

(3) **From Petroleum.** During World War II, the demand for toluene for the manufacture of explosives increased considerably, and

was met by a new process developed in 1940. This is based on the aromatization of *n*-heptane fraction (chap. 9, sec. 8, reac. 3, p. 143).—



n-Heptane

Toluene

The reaction involves cyclization and aromatization, and is carried out in the presence of a catalyst (oxides of chromium or molybdenum). Yield is very excellent, being about 70 per cent in one pass and 90 per cent on recycling.

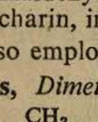
Properties. Toluene, like benzene, is a colourless, highly refracting mobile liquid with a characteristic aromatic odour. It boils at 110°, and freezes at −98°.

In chemical properties, toluene resembles other alkylbenzenes (sec. 4). The action of chlorine on toluene under various conditions has already been described (sec. 4). When treated with chromyl chloride in carbon disulphide solution, an addition compound having the formula $C_6H_5CH_3.2CrO_2Cl_2$, is obtained, which on being decomposed with water, yields benzaldehyde (**Etard's reaction**). When nitrated, toluene yields chiefly the *o*- and *p*-nitrolotoluenes, together with a much smaller proportion of the *m*-compound.

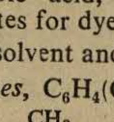
Uses. (1) Toluene is largely employed in the preparation of a large variety of aromatic derivatives, *e.g.*, benzyl chloride, benzal chloride, benzaldehyde, benzoic acid, novocaine, trinitrotoluene (T.N.T.), saccharin, intermediates for dyestuffs, etc.

(2) It is also employed as a solvent and in dry cleaning.

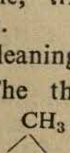
6. Xylenes, *Dimethylbenzenes*, $C_6H_4(CH_3)_2$.—The three xylenes,



o-Xylene
(*b. p.*, 142°)



m-Xylene
(*b. p.*, 139°)



p-Xylene
(*b. p.*, 138°)

are contained in coal-tar and the "light oil" derived from the coke-oven gas, and are obtained from them by fractional distillation. The "xylene fraction" consists of about 50 to 60 per cent of *m*-xylene and 10 to 25 per cent each of the ortho and para xylenes, together with a small proportion of ethylbenzene, $C_6H_5C_2H_5$ (*b. p.*, 134°). Since the boiling points of the constituents are so near each other, their separation[1] is difficult. Hence, for most technical purposes, the mixture is used as such.

---

[1] Special methods have now been worked out for effecting a separation. These are based on the differences in the readiness of sulphonation of the isomers and of desulphonation (hydrolysis) of the resulting sulphonic acids (compare sec. **2, method 5**).

The three xylenes may be synthesized by the general methods already described, and possess the general physical and chemical properties of alkylbenzenes. When submitted to oxidation, they first give the three monocarboxylic acids, $C_6H_4(CH_3)COOH$, called **toluic acids**, and then the corresponding dicarboxylic **phthalic acids**, $C_6H_4(COOH)_2$.

Uses :—

(1) The mixture of xylenes is used for the preparation of lacquers, and as solvents for rubber.

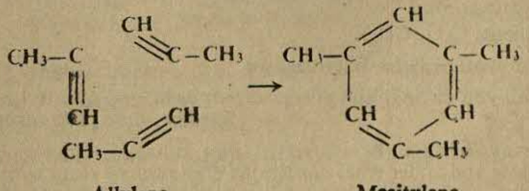
(2) Their amino derivatives are employed in the manufacture of dyes.

(3) *m*-Xylene is employed in the manufacture of "**xylene musk**".

7. **Hydrocarbons of the Formula C_9H_{12}.**—There are eight isomeric alkyl benzenes of the formula C_6H_{12}, *viz.*, three trimethyl-benzenes (1:2:3, 1:2:4, 1:3:5), three methylethylbenzenes (*o*-, *m*- and *p*-), one propyl-benzene, $C_6H_5CH_2CH_2CH_3$ and one isopropyl benzene, $C_6H_5CH(CH_3)_2$.

Mesitylene. *1:3:5*- or *s-trimethylbenzene* is the most important of the C_9H_{12} hydrocarbons. It occurs to a small extent in coal-tar, but is best obtained by distilling a mixture of acetone (2 vols.), concentrated sulphuric acid (2 vols.) and water (1 vol.). For equation, see page 280.

Another synthesis of this hydrocarbon consists in treating allylene[1] with concentrated sulphuric acid :



Allylene Mesitylene

The above syntheses of mesitylene are of importance, because they prove t hydrocarbon to possess a **symmetrical structure**, a fact that has been often used determining the orientation of benzene derivatives.

Mesitylene resembles other hydrocarbons of this series in its physical and chemical properties. It boils at 165°. When oxidized with dilute nitric acid, it yields successively *mesitylenic acid*, $C_6H_3(CH_3)_2COOH$, *uvitic acid*, $C_6H_3(CH_3)(COOH)_2$, and *trimesic acid*, $C_6H_3(COOH)_3$.

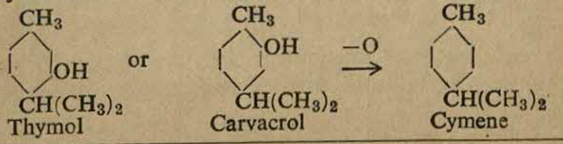
8. **Cymene.**—*p-Methyl-isopropyl-benzene*, is of considerable interest, as it is present in oil of thyme, oil of eucalyptus, and other ethereal oils and essences. It can be readily obtained by heating camphor with phosphorus pentoxide (dehydration):

$$C_{10}H_{16}O \rightarrow C_{10}H_{14} + H_2O$$

by heating turpentine oil with concentrated sulphuric acid (oxidation),

$$C_{10}H_{16} + O \rightarrow C_{10}H_{14} + H_2O$$

or by heating thymol or carvacrol with phosphorus pentasulphide (reduction) :



Thymol Carvacrol Cymene

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[1] Compare the synthesis of benzene from acetylene.

Cymene is a pleasant-smelling liquid, *b. p.*, 75°. On oxidation with dilute nitric acid, it yields *p*-toluic acid, $C_6H_4(CH_3)COOH$ and terephthalic acid, $C_6H_4(COOH)_2$.

9. Benzene Hydrocarbons with Unsaturated Side Chains.—Examples of this class of hydrocarbons are **phenylethyleaene** or **styrene,** $C_6H_5.CH{=}CH_2$, and **phenyl-acetylene,** $C_6H_5C{\equiv}CH$. They possess the properties characteristic of aromatic compounds as well as those of the unsaturated aliphatic hydrocarbons.

QUESTIONS

1. Give the general methods for the preparation of homologues of benzene. Discuss the action of oxidizing agents on these hydrocarbons.

2. How is toluene obtained on a large scale? Give an account of the properties and uses of toluene. (*Travancore, B.Sc., 1956*)

3. A hydrocarbon of the formula C_8H_{10} yields, on oxidation, a colourless crystalline dibasic acid containing 57·8 per cent carbon and 3·6 per cent hydrogen. The silver salt contains 56·1 per cent of silver. On heating the acid, it is converted into a compound of the formula $C_8H_4O_3$: on distillation with lime, benzene is formed. Discuss the structure of the original compound. (*Manchester, B Sc.*, ; *Punjab, B Sc.*)

[*Ans.* *o*-Xylene]

4. 0·2797 gm. of a liquid hydrocarbon gave, on combustion, 0·9364 gm. CO_2 and 0·2190 gm. H_2O. The vapour density of the hydrobarbon was found to be 46. On oxidation, it gave an acid having the empirical formula $C_7H_6O_2$. What is the hydrocarbon ?

(*Ans.* Toluene, $C_6H_5.CH_3$).

5. Give the synthesis of *n*-Butylbenzene. (*Lucknow, B Sc., 1961*)

6. How will you distinguish between *ortho*, *meta*, and *para* xylenes ? (*Bombay, B.Sc., Chemistry, Sub., 1962*)

7. How may benzene be converted into toluene, and thence into benzaldehyde ? How and under what conditions does toluene react with (*a*) chlorine, (*b*) nitric acid ? (*Oxford University*)

8. State how you would distinguish between the isomeric aromatic hydrocarbons of the formula C_8H_{10}. How will you show that they are all derivatives of benzene ? Describe a method for the separation of the isomeric xylenes. (*Lucknow, B.Sc., 1956*)

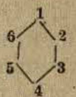
9. How is toluene obtained from :—(*i*) Coal-tar ; and (*ii*) benzene ? Describe the important properties and uses of toluene. (*Mysore, B.Sc., 1962*)

CHAPTER THIRTY-NINE

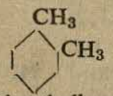
SUBSTITUTION IN BENZENE NUCLEUS

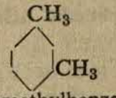
1. Isomerism of Benzene Derivatives.—Owing to the equivalence of six hydrogen atoms, the mono-substitution products of benzene exist only in one form. Thus, there is only one monochloro-benzene, C_6H_5Cl, one monobromo-benzene, C_6B_5Br, and so on.

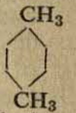
When two or more hydrogen atoms of benzene are replaced by substituents, the relative position of the latter are best denoted by numbers as shown in the margin.



The disubstitution products of benzene occur in *three* forms shown below in the case of xylenes (dimethylbenzenes) :


1,2-Dimethylbenzene
or *ortho*-Xylene

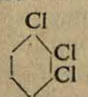

1,3-Dimethylbenzene
or *meta*-Xylene

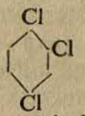

1,4-Dimethylbenzene
or *para*-Xylene

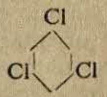
The terms **ortho-**, **meta-**, and **para-** are applied to 1,2-, 1,3- and 1,4- compounds respectively. For the sake of brevity, they are denoted by the letters *o*-, *m*- and *p*-.

Even when the two substituents are different, the number of isomerides remains three. Thus there are three chloromethylbenzenes three chlorobromobenzenes, and so on.

When three hydrogen atoms of the benzene nucleus are replaced, the case is otherwise. Thus tri-substitution products in which all the substituents are *identical*, exist in three forms, designated as shown below :

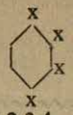

Vicinal
vic- or 1,2,3-
trichlorobenzene

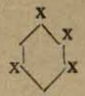

Asymmetrical,
as- or 1 2,4-
trichlorobenzene

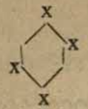

Symmetrical,
s- or 1,3,5-
trichlorobenzene

In case two of the three substituents are identical, as in $C_6H_3(OH)Br_2$, six isomerides are possible; if all three are different, as in $C_6H_3(OH)ClBr$, the number of the possible isomerides becomes ten.

The tetra-substitution products of benzene, in which all the substituents are identical, also exist in three isomeric forms as shown below ;


1,2,3,4-

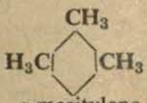

1,2,3,5-


1,2,4,5-

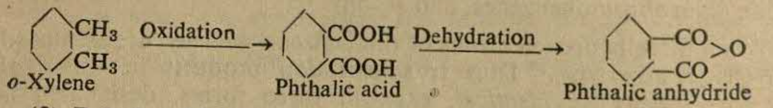
When five or six atoms of hydrogen are replaced by identical substituents, there is again only one compound possible. If the substituents be different, the number of possible isomers in each case becomes much higher.

2. Orientation of Substituents in Benzene Derivatives.—The determination of positions of substituents in the benzene nucleus is called *orientation*. There are two general methods of orientation, *viz.*, the *relative* method and the *absolute* method. Besides these two, certain *special* methods have sometimes proved useful.

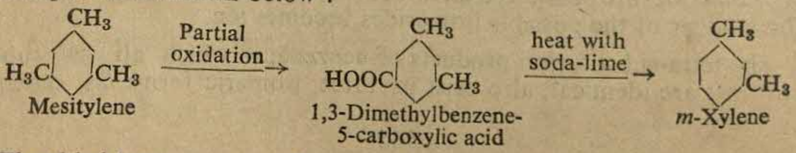
(1) **Special Methods.** We may cite two specific examples under this category, *viz*, (*i*) the orientation of **mesitylene** (1,3,5-trimethylbenzene) and (*ii*) that of **phthalic acid** (benzene-1,2-dicarboxylic acid). The former is based on the *synthesis* of the compound from acetone (p. 280) and from allylene (p. 563). The orientation of phthalic acid follows from its *chemical behaviour* on heating. Out of the three benzene dicarboxylic acids that are known, only the phthalic acid gives the anhydride on heating. The other two are not decomposed. Hence, in phthalic acid the two carboxyl groups must be attached to two *neighbouring* carbon atoms of the benzene ring (compare succinic acid, which also gives an anhydride). In other words, phthalic acid is benzene-*ortho*-dicarboxylic acid.



s-mesitylene



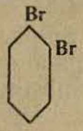
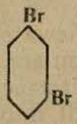
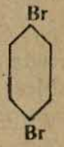
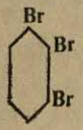
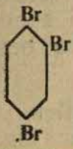
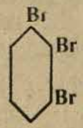
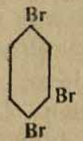
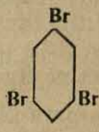
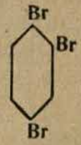
(2) **Relative Method.** In this method, the orientation of substituents in the compound is determined by reference to substances of *known* orientation. We may take the orientation of the **three xylenes** as an example. When submitted to oxidation, one of these gives phthalic acid which forms a cyclic anhydride on heating. This particular xylene must therefore be the *ortho*-compound. The dicarboxylic acids obtained from the other two xylenes do *not* form anhydrides. One of the remaining two xylenes can be obtained from *mesitylene* (1,3,5-trimethylbenzene), and must therefore be the *meta*-compound as shown below :



The third isomer must, of course, be the *para*-compound.

Though in most reactions it has been found that the positions of the substituents remain unaltered, a few cases are known where the position of a substituent does alter[1]. Hence, in a doubtful case it is necessary to check the determination of position by converting the substance into another compound.

(3) **Korner's Absolute Method.** In Korner's absolute method of orientation, the position of the substituent is determined *without* the aid of other compounds with substituents in known positions. The method is based on the fact that if a disubstitution product of benzene be converted into a trisubstitution derivative by further replacement of nuclear hydrogen, the para-compound would give only one trisubstitution product, the ortho- would give a mixture of two, while the meta- would give a mixture of three. Thus, the three bromobenzenes, on further bromination, yield the following trisubstitution products :

Dibromo-benzenes	 Ortho 1,2	 Meta 1,3	 Para 1,4
Tribromo-benzenes	 	  	

Korner's absolute method may also be employed for the orientation of the trisubstitution derivatives, as will appear from the scheme given on p. 568 :

The main difficulty of the method is that under the practical conditions some of the isomers may be produced in such small proportion as to make their detection almost impossible (see, however, foot-note, page 570). If this difficulty does not arise, the method is ideal.

3. Two Types of Aromatic Substitutions. The substitution reactions in the aromatic series may be divided into two distinct types :—

(*i*) *Normal or Non-reversible Substitutions.* Nitration and halogenation are characterized by being non-reversible reactions. The course taken by such reactions is mainly determined by the substituents already present in the benzene nucleus (sec. 4).

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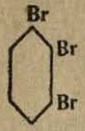
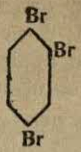
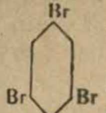
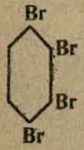
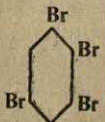
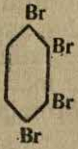
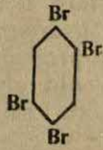
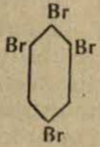
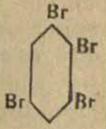
[1] Thus each of the three bromobenzene sulphonic acids, $C_6H_4Br(SO_3H)$, on fusion with potassium hydroxide, yields resorcinol (*m*-dihydroxybenzene). Similarly, in chloro- and bromo-phenols, a shifting of position of the substituents occurs on fusion with alkalis.

Tribromo-benzenes	 1,2,3	 1,2,4	 1,3,5
Tetrabromo-benzenes	 	  	

(*ii*) *Abnormal or Reversible Substitutions.* Sulphonation and Friedel-Crafts' alkylation are reversible reactions, and are markedly subject to the effect of temperature. The *ortho* substitution in such reactions occurs, if at all, only at low temperatures.

4. Directive Influence of Substituents in Normal Substitutions.— The nature of a substituent already present in the benzene nucleus exerts a profound control over (*i*) the position taken up by the new entrant and (*ii*) the ease with which the reaction occurs. From this point of view, the groups already present in the benzene nucleus fall into two distinct types :

(1) **Ortho-para-directing Groups ; Activation.** The following groups, when already present in the benzene ring, direct the newly entering substituents to the *ortho* and *para* positions ; and are consequently called *ortho-para-directing groups* or **ortho-para-directors** :—

$-NH_2$ $-OH$ $-OCH_3$ $-NHCOCH_3$
$-Cl$ $-Br$ $-I$ $-CH_3$

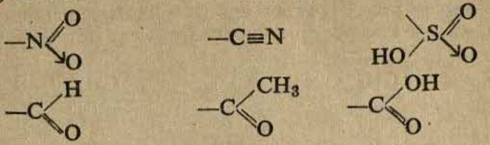
The points to be carefully noted in connection with the ortho-para substitution are :

(*a*) In each of the ortho-para directing groups, the atom through which the group gets attached to the carbon of the benzene nucleus is *covalently saturated.*

(*b*) The $-NH_2$ and $-OH$ groups, which have the most powerful ortho-para directing influence, also possess a very marked **activating effect** on the substitution reactions. The remaining groups (with the exception of the halogen substituents) also have the same activating effect on the reaction, though to a lesser degree.

(*c*) The halogen atoms resemble the other groups only so far as the ortho-para directing effect is concerned. They, however, render substitution somewhat *more difficult*. In this latter respect, they resemble the *meta*-directing groups.

(2) **Meta-directing Groups ; Deactivation.** The groups listed below direct the newly entering substituents to the *meta* position. They are, therefore, termed *meta-directing groups* or **meta directors** :—

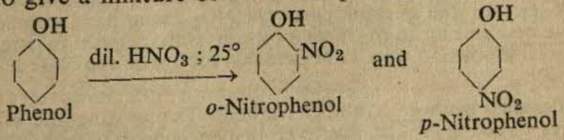


The following points may be noted in connection with meta substitutions :—

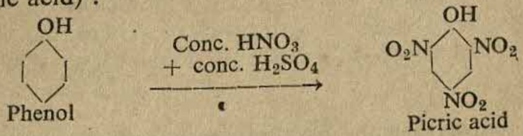
(*a*) The atom through which the meta-directing group is attached to the aromatic nucleus is *covalently unsaturated.*

(*b*) The meta-directing groups tend to **deactivate** the whole ring so that the substitution is considerably retarded. The above list is arranged in the order of decreasing effectiveness, the $-NO_2$ group being the most powerful in this respect and the carboxyl group the least so.

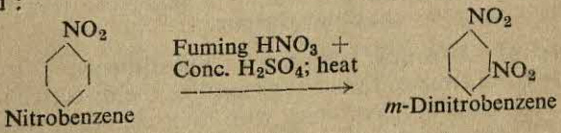
Examples. (1) Phenol is nitrated *very easily* even with cold dilute nitric acid to give a mixture of *ortho* and *para* nitrophenols :



When treated with a mixture of concentrated nitric and sulphuric acids, a vigorous reaction sets in, with the formation of 2,4,6-trinitrophenol (picric acid) :



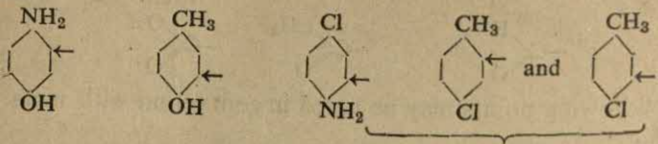
(2) Nitrobenzene can be nitrated to *m*-dinitrobenzene only by heating with a mixture of fuming nitric acid and concentrated sulphuric acid :



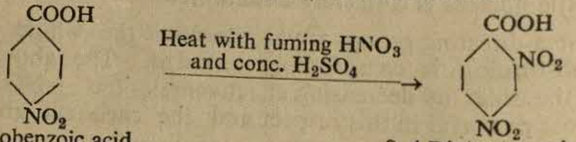
5. Relative Effectiveness of Directing Groups.—

(1) **Competition method.** The effectiveness of two *ortho-para* directing groups is compared by arranging a sort of *competition* between the two groups. This is done by starting with a disubstituted benzene derivative having the two groups to be compared in the *para* position to each other, and submitting it to various substitution reactions. The position occupied by the new entrant decides the matter. Thus, if we start with *p*-aminophenol, the substitution occurs with the new entrant going to the *ortho position with respect to the amino group.* The amino

group, therefore, has a greater effectiveness than the hydroxyl group. From the scheme given below, in which the position of the new entrant is indicated by an arrow, it follows that the NH_2 group is the most effective of all, the OH group comes next, while the CH_3 and the Cl are the least effective. The difference between the effectiveness of the CH_3 group and the Cl is so small that *p*-chlorotoluene yields a *mixture* of the two possible monosubstituted derivatives in about equal proportions :



The relative effectiveness of *meta*-directors may be determined similarly. Thus, on nitrating *p*-nitrobenzoic acid, we get 2,4-dinitrobenzoic acid :

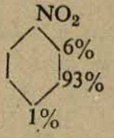


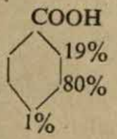
p-Nitrobenzoic acid

2, 4-Dinitrobenzoic acid

Hence, we see that the nitro group is a stronger meta-director than the carboxyl group. It may be recalled that the presence of a meta-directing group in the benzene ring deactivates all the remaining positions, particularly the *ortho* and the *para* ones. In the present case, the NO_2 group has succeeded not only in directing the new entrant to the meta position with respect to itself but also in keeping its ortho-position free. The carboxyl group, on the other hand, has failed to do so.

(2) **Holleman's method.** Another method of comparing the effectiveness of various meta-directing groups, due to Holleman, consists in finding the exact proportions[1] of the isomers produced on nitration. The percentages are conveniently recorded in the formula of the starting compound itself, as shown below for nitration of nitrobenzene and benzoic acid :





From the formula and the recorded figures we see that nitrobenzene on further nitration gives a mixture of the three dinitrobenzenes in the ratio : *ortho* 6 per cent, *meta* 93 per cent, *para* 1 per cent. The nitration of benzoic acid, on the other hand, gives a mixture of the three nitrobenzoic acids in the ratio : *ortho* 19 per cent, *meta* 80 per cent, *para* 1 per cent. The nitro group, therefore, is a much stronger meta-director than the carboxyl group.

6. Rules of Orienting Influence of Substituents.—Attempts have been made from time to time to generalize the directive influence of various substituents in accordance with their chemical behaviour or structure. These rules, though empirical and not universally applicable, have been found to be of practical utility.

(1) **Crum Brown-Gibson Rule** (1892). This rule states that if a substituent, *X*, already present in the benzene nucleus, forms with

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[1] This is done by *thermal analysis i.e.*, by the use of melting-point curves of mixtures of the products in various proportions.

hydrogen a compound, *HX*, which can be *directly* oxidized to the corresponding hydroxy-compound, XOH, the new entrant will take up the *meta* position with respect to *X*. Otherwise, it will take up the *ortho* and the *para* positions. Thus, in the case of NO_2 group the hydrogen compound HNO_2 is directly oxidizable to HNO_3. Hence this group has the meta-directive influence. On the other hand, the hydrogen compound NH_3 derived from the NH_2 group is not directly oxidizable to NH_2OH, and so NH_2 is one of the ortho-para directors.

The following table illustrates the applicability of the Crum Brown-Gibson rule :—

Substituent —X	Hydrogen compound, HX	Hydroxy compound, XOH	XOH producible by direct oxidation of HX or not	Directive influence of —X
$—NO_2$	HNO_2	HNO_3	Yes	Meta
$—SO_3H$	H_2SO_3	H_2SO_4	"	"
—COOH	HCOOH	H_2CO_3	"	"
—OH	H_2O	H_2O_2	No	Ortho-para
$—NH_2$	NH_3	NH_2OH	"	"
—Cl	HCl	HOCl	"	"

(2) **Vorlander's Rule.** According to this rule, if the atom, through which the substituent group is attached to the carbon of the benzene ring, is *covalently saturated* (*e.g.*, N of the $—NH_2$ group, O of the —OH group and C of the $—CH_3$ group), the group will have the *ortho-para* directive influence on the new entrant. If, on the other hand, it is covalently unsaturated (*e.g.*, N of the $—NO_2$ group, S of the $—SO_3H$ group and C of the —COOH group), the substituent will be a meta director.

(3) **Hammick-Illingworth Rule** (1930). This rule states that in the case of a monosubstituted benzene derivative —XY, in which the substituent group XY is attached to the carbon of the benzene nucleus through the atom X, while Y is an atom directly attached to X, *if Y is in a higher group in the periodic table, or if, being in the same group, it has a lower atomic number, the group XY will be a meta-director.* In other cases, including one-atom substituents (*e.g.*, Cl and Br), an ortho-para directive influence is exerted. Thus, in the case of the NO_2 group, the oxygen is in the higher periodic group (group VI) than nitrogen (group V), so the nitro-group is a meta-director. In the case of the $—SO_3H$ group, oxygen belongs to the same periodic group as sulphur (viz., group VI) but it has a *lower* atomic number. So, here too the group directs the new entrant to the *meta* position. On the other hand, the $—NH_2$ and —OH groups have an *ortho-para* directing influence, as hydrogen belongs

to a lower periodic group (group I) than nitrogen (group V) and oxygen (group VI).

The following table illustrates the Hammick-Illingworth rule :—

Substituent —XY	Group No. of X	Group No. of Y	Directive influence of —XY
$-NO_2$	V	VI	Meta
$-SO_3H$	VI	VI	,,
—COOH	IV	VI	,,
—OH	VI	I	Ortho-Para
$-NH_2$	V	I	,,
$-CH_3$	IV	I	,,
—Cl	VII	—	,,

Exceptions.—These rules, though applying in most cases, are subject to exceptions. Thus, cinnamic acid, $C_6H_5CH=CH.COOH$, on nitration yields ortho- and para-nitro derivatives. Further, the normal directive influence of COOH and $-NH_2$ groups is largely reversed by salt formation. Thus sodium benzoate, C_6H_5COONa, when chlorinated in aqueous solution yields ortho- and para-chloro derivatives. Similarly, aniline, $C_6H_5NH_2$, when nitrated in the presence of a large excess of sulphuric acid, gives mostly *meta*-nitraniline.

QUESTIONS

1. What do you understand by the term "Orientation" ? Explain with the aid of examples how this has been carried out in the case of di- and tri-substitution products of benzene. (*Travancore, B.Sc., 1942*)

2. Write a short note on Korner's absolute method of orientation. (*Calcutta, B.Sc., 1953*)

3. Write an essay on the 'directive influence' of substituents on further substitution in the benzene ring. Show what compounds are formed when (*a*) toluene, (*b*) phenol, (*c*) benzaldehyde, (*d*) benzoic acid and (*e*) *m*-xylene are nitrated. (*Banaras, B.Sc., 1954*)

4. State clearly the rules describing the positions taken by substituents introduced into benzene derivatives. Applying the rules stated above, predict what products will be formed in the following reactions :—

(*i*) Ethylbenzene and nitric acid, (*ii*) Ethylbenzene and bromine in the presence of ferric bromide, (*iii*) Nitrobenzene and sulphuric acid, (*iv*) Para-cresol and sulphuric acid, and (*v*) Benzenesulphonic acid and bromine. (*Rajputana, B.Sc., 1954*)

5. Describe how the relative effectiveness of two or more ortho-para-directing groups may be determined ? On heating *p*- nitrobenzoic acid with a mixture of fuming nitric acid and concentrated sulphuric acid, 2,4-dinitrobenzoic acid is obtained as the major product. What conclusion do you draw as to the relative efficiency of the nitro and the carboxyl groups as meta directors ?

6. State Crum Brown-Gibson and Hammick-Illingworth rules of substitution in the benzene nucleus. Give concrete examples to illustrate these rules. Do you know any case or cases where the results obtained contradict the rules ?

7. Write a short note on Orientation of Benzene Derivatives. (*Lucknow, B.Sc., 1959*)

8. Write an account of the various theories that have been put forth to account for the directing influences of substituents in the benzene ring. (*Bombay, B.Sc., 1956*)

9. Write an essay on Aromatic Substitution. (*Gujarat, B.Sc., 1957*)

10. Write an essay on the Directive influence of substituents on further substitution in the benzene ring. Show what compounds are formed when (*a*) toluene, (*b*) phenol, (*c*) benzaldehyde, and (*d*) benzoic acid are nitrated. (*Punjab, B.Sc. Dairying, 1960*)

11. Explain methods of determining the positions of the substituents in the disubstituted products of benzene. What is meant by "orienting influence" of a substituent group ? (*Mysore, B.Sc., 1960*)

12. Write an account of Orientation of groups in the benzene ring. (*Lahore, B.Sc., 1962*)

13. Give an account of the laws of substitution in the benzene ring. (*Patna, B.Sc., 1960*)

14. (*a*) What do you mean by the term 'Orientation' ? Give the Korner's orientation method.

(*b*) Illustrate by examples how in Aromatic Compounds further substitution is governed by the nature of the substituent already present in the ring. (*Punjab, B.Sc., 1963*)

15. Write a note on Korner's absolute method of orientation. (*Poona, B.Sc., Second Year, 1961*)

16. Write a note on "Orientation of Substituents in Benzene". (*Madras, B.Sc., Chemistry-Main, 1963*)

CHAPTER FORTY

ELECTRONIC THEORY OF AROMATIC SUBSTITUTIONS

1. General.—Electronic concept of the mechanism of substitution in the aromatic nucleus, first introduced by the well-known English chemists Lapworth, Robinson and Ingold during the years 1920—34, is based on the following factors :

(1) **Inductive Effect.** One important basic factor of the modern theory is that the electrons constituting a heteropolar[1] covalent bond are shared *unequally* by the atoms concerned. This condition is usually represented by a line marked with an arrow-head, showing the **direction** of the electron shift. Thus, the carbon-chlorine bond, C—Cl, is symbolized as C→—Cl, which implies permanent polarization of the bond. The polarization, however, is not restricted to the bond itself; it tends to be transmitted along a saturated chain, C→—C→—C→—Cl. This induced polarization along the saturated chain is called the **inductive effect.** It must be clearly understood, however, that the inductive effect does not bring about any actual transfer of electrons from one atom to another: It merely serves to bring into existence certain centres of reactivity, without in any way affecting the usual valencies of the atoms constituting the chain.

The inductive effect of an atom, or group, falls off rapidly with distance, until it gets completely damped out.

(2) **Resonance or Mesomeric Effect.** The electron movements are of particular importance in the case of compounds containing double or triple bonds. Here, they have a greater scope than in the case of single-bond, saturated compounds. We already had an opportunity to mention the phenomenon of resonance or mesomerism in connection with the general discussion of molecular structure (p. 79, sec. 22). We noted there that the compounds capable of exhibiting resonance are more stable than they could otherwise be. We discussed at some length the mesomeric structures of CO_2 and ethylene (p. 80). Other important examples of resonance are provided by the carboxyl group (page 307) and the benzene ring (p. 556).

(3) **Dipole Moments.** The significance of this important property of the molecule has already been discussed (p. 98). The group dipole moments of benzene derivatives[2] in benzene solution at 25° are listed

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[1] *i.e.*, a bond between unlike atoms.

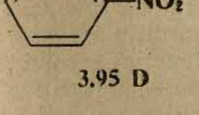
[2] The dipole moment of benzene itself is zero.

in the margin.

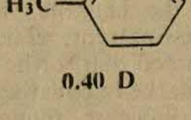
The dipole moment is the most directly useful physical property for investigating molecular structure, and is of particular interest in explaining aromatic substitution and the orienting effect that a substituent exercises on a new entrant in the ring. While the *magnitude* of the inductive effect of a substituent is given by the dipole moment of the monosubstituted benzene, its *direction* is determined by a method of comparison in which a substituent of known direction of inductive effect is employed as a reference. The nitro group is perhaps the most suitable reference, as of its two component elements oxygen is decidedly the more electronegative than nitrogen and tends to pull the electrons of the heteropolar covalent bond away from the nitrogen.

	Substituent	μ in Debyes
Electron-attracting	$-NO_2$	3·95
	$-CN$	3·93
	$-COCH_3$	2·92
	$-CHO$	2·78
	$-COOCH_3$	1·9
	$-F$	1·43
	$-Cl$	1·55
	$-Br$	1·52
	$-I$	1·30
	$-COOH$	1·0
Electron-releasing	$-N(CH_3)_2$	1·58
	$-NH_2$	1·53
	$-OH$	1·60
	$-OCOCH_3$	1·52
	$-OCH_3$	1·16
	$-CH_3$	0·40

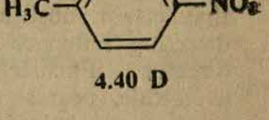
We may illustrate the method of comparison for establishing the direction of the inductive effect of the methyl group on the benzene nucleus. The experimental values of dipole moments of toluene, nitrobenzene and *p*-nitrotolune are 0·40, 3·95 and 4·40 respectively. The value for *p*-nitrotoluene is approximately equal to the *sum* of the values for toluene and nitrobenzene and not to the difference between the two. It therefore follows that if the nitro group at one terminal of the benzene ring *attracts* electrons, the methyl group at the other end must *repel* them. In other words, the two moments reinforce each other :



3.95 D



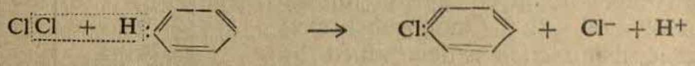
0.40 D

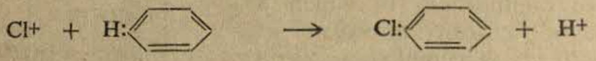


4.40 D

The groups capable of direct union with the benzene ring can, by this method of comparison; be divided into two classes : (*i*) **electron-attracting**, if they operate in the same direction as the nitro group, and (*ii*) **electron-releasing**, if they operate in the opposite direction. The table in the margin above indicates the class to which a particular substituent belongs. An electron-attracting group attached to the benzene nucleus induces a condition of low electron density in the nucleus, while an electron-releasing group has the opposite effect ; it brings about a high electron density in the ring.

2. Electrophilic and Nucleophilic Reactions.—An electron-sharing organic reaction may be "electrophilic" or "nucleophilic" according to the nature of the attacking reactant. A reagent capable of accepting electrons is termed *electrophilic* and the one capable of donating electrons *nucleophilic*. A substitution reaction brought about through electrophilic attack is termed an S_E **reaction** and one brought about through a nucleophilic attack an S_N **reaction**. A typical example of an S_E reaction is the chlorination of benzene, which may be represented in either of the following ways :

(*i*) 

(*ii*) 

In formulation (*i*), one of the chlorine atoms of the Cl:Cl bond is shown as becoming the chloride ion by retaining the electron pair of the bond. The other chlorine atom plays the role of an electrophilic fragment, and gets united with the benzene ring. The formulation (*ii*) represents the reaction as an electrophilic attack by the cation, Cl^+.

A familiar example of an S_N reaction is the hydrolysis of an alkyl halide by an alkali, which may be formulated as follows :

$$\text{Na:OH} + \text{R:Cl} \longrightarrow \text{R:OH} + Na^+ + Cl^-$$

or,

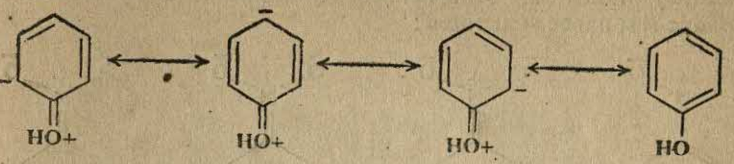
$$OH^- + \text{R:Cl} \longrightarrow \text{R:OH} + Cl^-$$

An attack by a cation or an electrophilic fragment of the reagent employed occurs at the point of the organic molecule where the electron availability is the maximum. Similarly, a nucleophilic attack is always at the point of minimum electron availability of the organic molecule.

3. Orienting Influence of Substituents already present in the Benzene Ring.—In sec. 4 of the preceding chapter (p. 568) we noted that certain substituents in the benzene ring exert an *ortho-para* directing influence on a new entrant, while certain others are *meta* directors. Further, it was noted that ortho-para directing groups, as a rule, possess a very marked activating effect on a substitution reaction. A halogen atom, however, though possessing an ortho-para directing influence, renders substitution somewhat *more difficult*. On the other hand, the *meta* directing substituents tend to deactivate the benzene ring, so that the substitution reaction is considerably retarded. We shall now attempt to explain these facts on the basis of electronic theory of organic reactions.

Ortho-Para Orientation.—

A powerful electron-repelling group, when attached to the benzene nucleus, produces high electron density at *ortho* and *para* positions through resonance, as shown below for phenol :

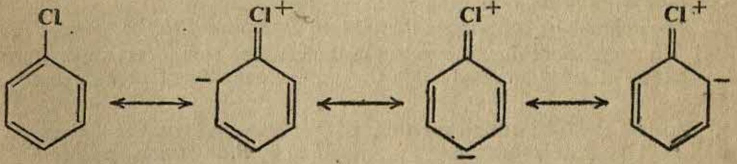


Hence, treatment of a monosubstituted benzene derivative of the phenol type with an electrophilic reagent will always occur at the *ortho* and the *para* positions. Further, the existence of strong negativity centres in the ring renders the electrophilic attack much more effective. This explains the *activating* influence of an ortho-para directing group on an aromatic substitution reaction.

Anomalous Behaviour of Halogen Substituents. Although a great majority of electron-attracting substituents direct a new entrant to the *meta* position, the halogen atoms constitute an exception. They resemble the electron-*repelling* groups and orient the new entrant to the *ortho* and *para* positions. This anomaly has been explained on the basis of interatomic distances[1]. The C—Cl distance in the case of chlorobenzene (1.70 angstrom) is appreciably shorter than in that of chloromethane (1.76 angstrom). This indicates a partial double-bond character for the C—Cl bond in chlorobenzene.[2] A parallel case is that of vinyl chloride, in which the shorter C—Cl bond distance and markedly low chemical reactivity of the halogen atom is explained on the basis of resonance between the two forms :

$$H_2C{=}CH{-}Cl \rightleftharpoons \overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}$$

Chlorobenzene resembles vinyl chloride both as regards the comparatively smaller carbon-chlorine bond distance and the inertness of the halogen atom. Hence, here too the existence of resonance must be postulated. The compound is regarded as a resonance hybrid of four structures :



Meta Orientation.—

Electron-attracting substituents when linked to the benzene nucleus direct a new entrant to the *meta* position. The phenomenon may be explained with reference to the nitro group, which is the only one of the *meta* directing groups for which resonance structure is definitely indicated. Nitrobenzene molecule is a hybrid of four possible resonance structures :

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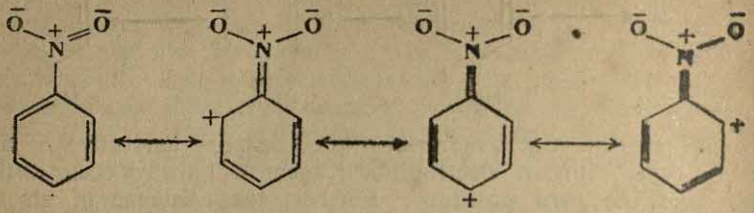
[1] Interatomic distances are determined by electron-diffraction method. (Refer to a textbook of Physical Chemistry.)

[2] A further indication of the existence of resonance in chlorobenzene is afforded by its smaller dipole moment (1·56 D) as compared with chloromethane (2·15 D).



The resonance leads to the establishment of *electropositive* centres at the *ortho* and the *para* positions, thus rendering them inaccessible for attack by electrophilic reagents.

The *meta* position too is deactivated for reaction, though to a much smaller extent. However, it is the only position that offers a somewhat better chance for electrophilic attack.

This explains the *meta* orienting and deactivating effect of an electron-attracting substituent, such as the nitro group.

QUESTIONS

1. Write an account of the electronic theory of aromatic substitution.

2. What do you understand ? by—(*i*) Inductive effect of a substituent (*ii*) Dipole moment of a molecule (*iii*) Resonance. How these phenomena are utilized for explaining certain aspects of aromatic chemistry ?

3. Write an account of the modern theory put forward to explain the directing influences of substituents in the benzene ring.

4. How do you distinguish between the electrophilic and the nucleophilic substitutions ? Give illustrative examples.

5. Explain the following facts on the basis of the electronic conception of chemical reaction :

(*i*) The OH group in direct union with the benzene nucleus activates the latter for further reaction, and, moreover, has an *ortho-para* directing influence on a new entrant into the ring.

(*ii*) The anomalous behaviour of a halogen atom linked to the benzene ring.

(*iii*) The presence of the nitro group in the benzene ring deactivates the ring and possesses a *meta* orienting influence on a substituent seeking entry into the ring.

6. Explain the substitution reactions of benzene and its derivatives on the basis of the theory of resonance. (*Madras, B.Sc., Chemistry-Main, 1960*)

7. Give a concise account of homolytic aromatic substitution. (*Madras, B.Sc., Chemistry-Main, 1961*)

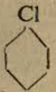
8. Give a brief account of substitution in the benzene ring with suitable examples. (*Madras, B.Sc., Chemistry-Main, 1962*)

CHAPTER FORTY-ONE

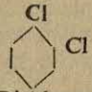
AROMATIC HALOGEN COMPOUNDS

1. Two Classes of Halogen Derivatives.—The halogen substitution products of benzene hydrocarbons belong to two distinct classes :—

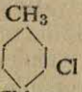
(*i*) **Aryl Halides.** These contain the halogen directly attached to the benzene nucleus ; *e.g.*,



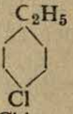
Chlorobenzene



o-Dichlorobenzene

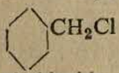


m-Chlorotoluene

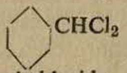


p-Chloroethyl benzene

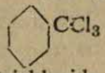
(*ii*) **Aryl-substituted Halides.** When the halogens replace the hydrogen of the side-chain of an alkylbenzene, we get a halogen derivative of an aryl-substituted aliphatic hydrocarbon. Thus, from toluene, $C_6H_5CH_3$, which may be regarded as *phenylmethane*, we get—



Benzyl chloride (monochlorophenylmethane)



Benzal chloride (dichlorophenyl methane)



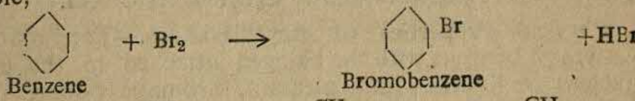
Benzotrichloride (trichlorophenylmethane)

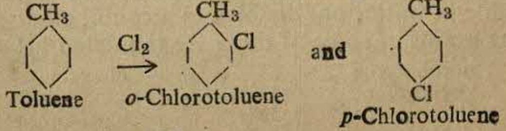
The two classes of derivatives differ from one another both in methods of preparation and in properties. The members of the second group, *i.e.*, those containing the halogen in the side-chain are, as a rule, very similar to the halogen derivatives of the aliphatic hydrocarbons.

2. Preparation of Aryl Halides.—The following methods are employed for the preparation of nuclear halogen derivatives :—

(1) **Direct action of chlorine and bromine.**

(*i*) *Nuclear Substitution.* When an aromatic hydrocarbon is treated with chlorine or bromine in the presence of a halogen carrier at the ordinary temperature, *chlorination* or *bromination* of the hydrocarbon occurs with the halogen replacing the hydrogen of the nucleus. For example,





The more important halogen carriers (*i.e.*, substances that accelerate halogenation catalytically) are iron, iodine, aluminium chloride, molybdenum chloride, etc. A mixture of iron and iodine has been found to be particularly active.

(*ii*) *Addition.* If a halogen carrier is not used, *addition compounds*, e.g., $C_6H_6Cl_6$ and $C_6H_6Br_6$, are produced in the cold.

(*iii*) *Side-chain Substitution.* At the boiling point and in the absence of a halogen carrier, substitution occurs in the side-chain. The presence of light and addition of peroxides also facilitate side-chain halogenation.

(2) **Iodination in presence of oxidizing agents.** The iododerivatives of benzene hydrocarbons *cannot* be obtained by the action of the halogen alone, because of strongly reducing action of the hydrogen iodide on the iodo-derivative first produced. Hence, the hydrocarbon is heated with iodine and an *oxidizing agent*, such as iodic acid or mercuric oxide, which oxidizes the hydriodic acid to iodine, and thus enables the reversible reaction,

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI,$$

to proceed to completion.

(3) **Bromination with hypobromous acid.** A simple method of brominating benzene derivatives, due to Stark, consists in shaking them with a cold aqueous solution of hypobromous acid. Derbyshire and Waters have developed a method (1950) for bromination with acidified bromine water in the presence of a silver or mercurous salt. Hypobromous acid is generated according to the equation,

$$H_2O + Br_2 \rightleftharpoons HOBr + HBr.$$

The silver and mercurous ions remove the bromide as the insoluble AgBr or Hg_2Br_2, and thus help the production of hypobromous acid.

(4) **Sandmeyer's reaction.** A very important general method for preparing aromatic halogen derivatives containing the halogen in the *nucleus,* consists in decomposing the solution of a diazonium salt. To obtain a chloro- or a bromo-derivative, the solution of the diazonium salt is warmed with a solution of cuprous chloride in hydrochloric acid, or a solution of cuprous bromide in hydrobromic acid, the cuprous salt simply acting as a catalyser :

$$C_6H_5N._2Cl \rightarrow C_6H_5Cl + N_2 \;.$$

$$C_6H_5{\cdot}N_2Cl + HBr \rightarrow C_6H_5Br + N_2 + HCl$$

For preparing the iodo-derivatives, no cuprous salt need be used as the catalyst; the reaction proceeds readily when the solution containing the diazonium salt is warmed with potassium iodide :

$$C_6H_5N_2Cl + KI \rightarrow C_6H_5I + N_2 + KCl.$$

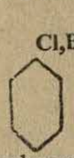
3. **Physical Properties of Aryl Halides.**—The monohalogen derivatives of benzene with the halogen attached to the carbon of the nucleus are liquids with a pleasant, aromatic odour. They are insoluble in water, but dissolve in alcohol, ether and benzene. The boiling points of some of them are tabulated below :—

Fluorobenzene	85°	*o*-Chlorotoluene	160°
Chlorobenzene	132°	*m*-Chlorotoluene	161·6°
Bromobenzene	156°	*p*-Chlorotoluene	162°
Iodobenzene	188°	*o*-Bromotoluene	182°

4. Chemical Properties.—

(1) **Inertness of the halogen atom—Drastic treatment necessary.** The halogen atom in the monohalogen derivatives of benzene is firmly bound, and, as compared with alkyl halides, is very unreactive. These compounds may be boiled with aqueous or alcoholic alkalis, potassium cyanide or potassium hydrosulphide without any reaction taking place.

However, drastic treatment with certain reagents may bring about substitution. The more important reactions of this category are summarized below :—



Chlorobenzene or bromobenzene

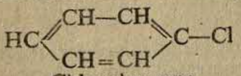
(i) $\xrightarrow{\text{NaOH, 300°}} C_6H_5OH$ (Phenol)

(ii) $\xrightarrow{\text{NaOCH}_3\text{, 220°}} C_6H_5OCH_3$ (Anisole)

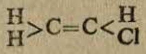
(iii) $\xrightarrow{\text{aqNH}_3\text{. (CuCl , 200°}} C_6H_5NH_2$ (Aniline)

(iv) $\xrightarrow[\text{presence of pyridine}]{\text{Heat with CuCN in}} C_6H_5CN$

The low reactivity of the halogen atom in a halogen derivative of benzene is comparable with that of a halogen derivative of an alkene in which the halogen atom is attached to a carbon carrying the double bond (*e.g.*, vinyl chloride). The similarity of structure of the two classes of compounds, as shown below, explains the similarity in chemical reactivity.



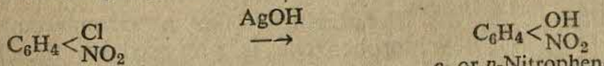
Chlorobenzene



$$\begin{matrix}H\\H\end{matrix}>C=C<\begin{matrix}H\\Cl\end{matrix}$$

Vinyl chloride

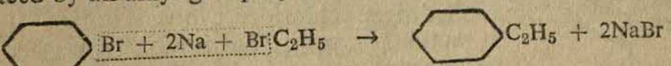
(2) **Activating effect of negative substituents.** The halogen atom linked to the aromatic nucleus is rendered very reactive by the presence of negative substituents, such as $-NO_2$, $-CN$, $-COOH$, in the *ortho* or *para* positions with respect to it. In fact, the halogen atom in such cases becomes as readily replaceable by the hydroxyl and the amino groups as in the alkyl halides ; *e.g.*,



$$C_6H_4<\begin{matrix}Cl\\NO_2\end{matrix} \xrightarrow{\text{AgOH}} C_6H_4<\begin{matrix}OH\\NO_2\end{matrix}$$

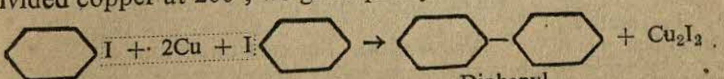
o- or *p*-Chloronitrobenzene *o*- or *p*-Nitrophenol

(3) **Wurtz-Fittig reaction.** A fact of considerable practical importance is that the halogen in the benzene nucleus may be readily replaced by an alkyl group by the Wurtz-Fittig Synthesis :



Ethyl benzene

(4) **Ullmann's reaction.** When iodobenzene is heated with finely-divided copper at 200°, we get diphenyl :



Diphenyl

This reaction recalls Wurtz-Fittig's synthesis of alkyl benzenes, but is of far greater general importance, as it can be applied to a variety of iodo- and bromo-substitution products of benzene, to give symmetrical diphenyl derivatives.

(5) **Grignard's reaction.** Another very important reaction of aryl halides is that, like alkyl halides, they react with dry metallic magnesium in the presence of dry ether to give **arylmagnesium halides**; *e.g.*,

$$\underset{\text{Phenyl bromide}}{C_6H_5Br} + Mg \longrightarrow \underset{\text{Phenylmagnesium bromide}}{C_6H_5MgBr}$$

This fact is of great practical importance, for these compounds, like the aliphatic organo-magnesium halides (chap. 13, page 215), find extensive application in synthesizing various classes of derivatives.

(6) **Addition of chlorine to iodo-derivatives.** Aromatic *iodo* compounds containing the halogen linked to the *nucleus* unite with two atoms of chlorine, yielding **iodochlorides.** The latter compounds when treated with an aqueous solution of sodium hydroxide yield **iodoso-derivatives,** the two chlorine atoms being replaced by an oxygen atom :

$$\underset{\text{Iodobenzene}}{C_6H_5I} \xrightarrow{+Cl_2} \underset{\text{Phenyl iodochloride}}{C_6H_5ICl_2} \xrightarrow{H_2O} \underset{\text{Iodosobenzene}}{C_6H_5IO}$$

5. Chlorobenzene, *Phenyl Chloride*, C_6H_5Cl.—This compound may be obtained by any of the general methods already described. In the laboratory, it is most conveniently prepared by the **Sandmeyer reaction.**

Aniline (1 part) is diazotised by means of sodium nitrite and concentrated hydrochloric acid (Chapter 44). The resulting cold solution of benzenediazonium chloride is gradually added from a tap funnel into a boiling solution of cuprous chloride (½ part) in concentrated hydrochloric acid (5 parts) contained in a round-bottom flask fitted with a reflux condenser (Fig. 1). When nitrogen ceases to be evolved, the chlorobenzene is separated by steam distillation, washed, dried and distilled.

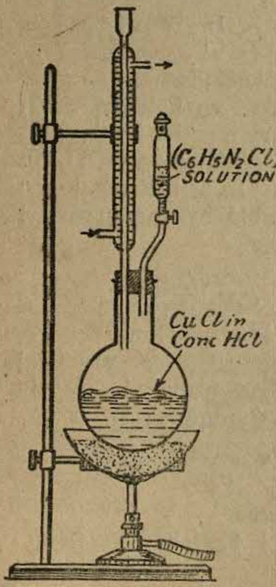


Fig. 1. Preparation of Chlorobenzene.

Manufacture. On a commercial scale, chlorobenzene is prepared by the chlorination of benzene. The reaction is carried out in an iron[1] vessel surrounded by a water jacket for cooling. The vessel is provided with an earthenware pipe through which the hydrogen chloride, evolved during the reaction, escapes. The product is washed with aqueous sodium hydroxide, dried and fractionally distilled to separate chlorobenzene from unchanged benzene and *o*- and *p*-dichlorobenzenes formed simultaneously.

Properties. See sections 3 and 4.

---

[1] Iron acts as the catalyst. The chlorine being dry, does not attack the vessel.

Industrial Uses.—

(1) Very large quantities of chlorobenzene are used for the manufacture of **phenol** and **aniline.**

$$C_6H_5Cl \xrightarrow{\text{NaOH, 300°}} C_6H_5OH \text{ (Phenol)}$$

$$C_6H_5Cl \xrightarrow{\text{Aq. } NH_3\text{, } (CuSO_4)\text{, 200°}} C_6H_5NH_2 \text{ (Aniline)}$$

(2) A fairly large proportion of chlorobenzene is submitted to nitration when a mixture of *p*-**chloronitrobenzene** (70 per cent) and *o*-**chloronitrobenzene** (30 per cent) is obtained. Further nitration of either isomer, or the mixture of two, gives **1-chloro-2,4-dinitrobenzene.**

(3) Manufacture of D. D. T. (see sec. 9).

6. **Bromobenzene,** C_6H_5Br.—This compound may be prepared from benzenediazonium chloride by Sandmeyer's reaction, using a solution of cuprous bromide in hydrobromic acid. It is usually prepared by the direct bromination of benzene in the presence of metallic iron or aluminium-mercury couple.

Dry benzene (1 part) and aluminium-mercury couple (one-hundredth part) is placed in a flask provided with a reflux condenser and a tap-funnel. To the top of the condenser is attached a bent tube for leading off hydrogen bromide into water contained in a beaker (see Fig. 2). Dry bromine (2 parts) is gradually dropped in from the tap-funnel. When the mixture has cooled, it is washed successively with dilute sodium hydroxide solution and water, dried, and finally fractionated, the fraction passing between 140° and 170° being collected separately.

Bromobenzene closely resembles chlorobenzene in physical and chemical properties. It boils at 155°.

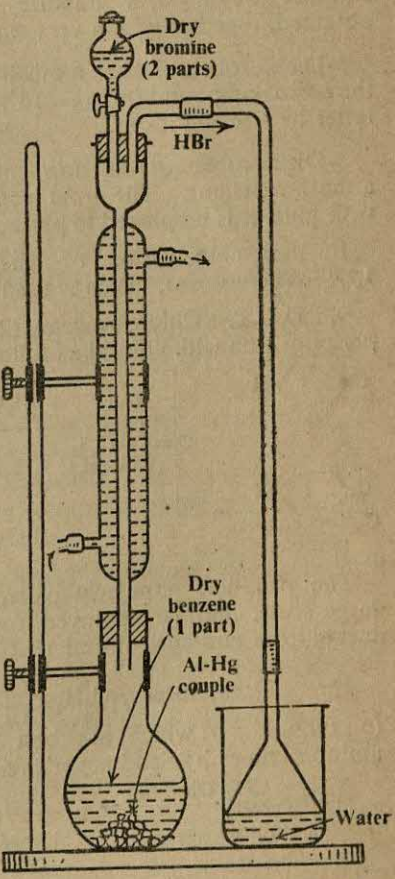


Fig. 2. Bromination of Benzene.

7. **Iodobenzene,** C_6H_5I.—This compound may be obtained by heating benzene with iodine and iodic acid. It is most conveniently prepared by decomposing benzenediazonium sulphate with aqueous potassium iodide :—

$$C_6H_5N_2SO_4H + KI \rightarrow C_6H_5I + N_2 + KHSO_4$$

Aniline (1 part) is diazotized by means of sodium nitrite and dilute sulphuric acid. The resulting cold solution of benzenediazonium sulphate is added to a concentrated solution of potassium iodide (2 parts) and the mixture is heated on a water-bath, until the evolution of nitrogen has ceased. The liquid is submitted to steam distillation to separate iodobenzene, which is then washed with dilute sodium hydroxide, dried and distilled.

Iodobenzene is a heavy (sp. g. 1·86), colourless liquid (*b.p.* 188°). When treated with chlorine it yields benzene iodochloride.

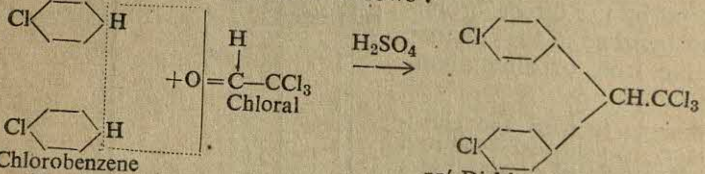
8. Di- and Tri-chlorobenzenes.—When benzene is submitted to chlorination at a slightly higher temperature in the presence of ferric chloride as catalyst, a mixture *ortho* and *para* **dichlorobenzenes** is obtained, together with a very small quantity of the meta compound.

p-Dichlorobenzene has a much higher melting point (53°C) than the *ortho* compound (*m. p.*,—18°), and is readily separated from the latter by freezing it out.

p-Dichlorobenzene is now much used instead of naphthalene as a moth repellant. The *ortho* isomer is a useful insecticide ; mixed with glue, it is employed to protect wood-work against boring insects.

Further chlorination of dichlorobenzenes yields principally **1,2,4-trichlorobenzene**, which is used in the control of white ant.

9. D.D.T.—Chlorobenzene (2 moles) readily condenses[1] in the *para* position with chloral as follows :—

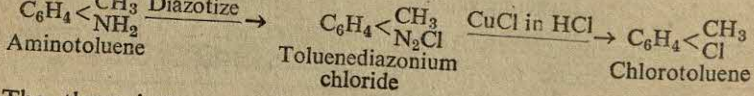


Chlorobenzene (2 moles)

pp'-Dichlorodiphenyl-trichloro methyl-methane (D.D.T.)

The product, popularly called D.D.T., is manufactured on a large scale, and is employed for exterminating flies, moths, lice, mosquitoes and agricultural pests.

10. Chlorotoluenes, $C_6H_4{<}\begin{smallmatrix}CH_3\\Cl\end{smallmatrix}$.—There are three chlorotoluenes (*o*-, *m*-, and *p*-) which are best prepared from the corresponding aminotoluenes by Sandmeyer's reaction :



$$C_6H_4{<}\begin{smallmatrix}CH_3\\NH_2\end{smallmatrix} \xrightarrow{\text{Diazotize}} C_6H_4{<}\begin{smallmatrix}CH_3\\N_2Cl\end{smallmatrix} \xrightarrow{\text{CuCl in HCl}} C_6H_4{<}\begin{smallmatrix}CH_3\\Cl\end{smallmatrix}$$

Aminotoluene Toluenediazonium chloride Chlorotoluene

The three isomers boil at 156°, 150°, and 156° respectively, and resemble chlorobenzene in most respects. On being oxidized, they give the corresponding *chlorobenzoic acids*, $C_6H_4ClCOOH$.

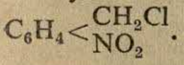
---

[1] This is one of the common condensation reactions that occur between aldehydes and nuclear hydrogen atoms of aromatic compounds.

11. Benzyl Chloride, $C_6H_5CH_2Cl$.—Benzyl chloride is a typical example of a halogen aromatic derivative containing the halogen atom in the *side-chain*. It may be obtained from benzyl alcohol, $C_6H_5CH_2OH$, by treatment with phosphorus pentachloride, but is always prepared by passing chlorine through boiling toluene.

It is a colourless liquid (*b.p.* 178°) with an unpleasant smell, and has a powerful irritating effect on the eyes and nose.

Reactions. (1) Like other aromatic derivatives, it can be readily nitrated, and gives a mixture of isomeric nitro-compounds,



$$C_6H_4<\begin{matrix}CH_2Cl\\NO_2\end{matrix}.$$

(2) With boiling water, it yields benzyl alcohol,

$$C_6H_5CH_2Cl + HOH \rightarrow C_6H_5CH_2OH + HCl,$$

with alcoholic ammonia, benzylamine,

$$C_6H_5CH_2Cl + NH_3 \rightarrow C_6H_5CH_2NH_2 + HCl,$$

and with silver acetate, benzyl acetate :

$$C_6H_5CH_2Cl + CH_3COOAg \rightarrow CH_3COOCH_2C_6H_5 + AgCl.$$

(3) The behaviour of benzyl chloride towards oxidizing agents is of great practical importance. When heated with 60 per cent nitric acid, it yields benzoic acid :

$$C_6H_5CH_2Cl + 2HNO_3 \rightarrow C_6H_5COOH + H_2O + HCl + N_2O_3$$

The reaction is employed on a large scale for the manufacture of benzoic acid.

When benzyl chloride is boiled with an aqueous solution of lead nitrate (or cupric nitrate) benzaldehyde is obtained :

$$2C_6H_5CH_2Cl + Pb(NO_3)_2 \rightarrow 2C_6H_5CHO + H_2O + PbCl_2 + N_2O_3$$

The reaction is employed for the preparation of benzaldehyde in the laboratory and on a commercial scale.

Uses. As already mentioned, benzyl chloride is employed in the manufacture of benzoic acid and benzaldehyde.

12. Benzal Chloride or *benzylidene chloride*, $C_6H_5.CHCl_2$, (*b.p.* 207°) and **benzotrichloride**, $C_6H_5.CCl_3$, (*b.p.* 213°) are both obtained by the prolonged action of chlorine on boiling toluene. They may be separated from the mixture by fractional distillation.

Uses. Benzal chloride and benzotrichloride are both employed industrially, the former in the preparation of benzaldehyde and the latter in that of benzoic acid. In practice, the mixture of the two derivatives, obtained as above, is heated under pressure with milk of lime, without previous separation, when we get benzaldehyde and the calcium salt of benzoic acid :

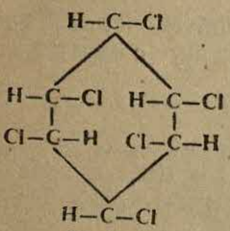
$$C_6H_5CHCl_2 \xrightarrow{HOH} \underset{\text{(unstable)}}{C_6H_5CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

$$C_6H_5CCl_3 \xrightarrow{HOH} \underset{\text{(unstable)}}{C_6H_5C(OH)_3} \xrightarrow{-H_2O} C_6H_5COOH \xrightarrow{Ca(OH_2)} \underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca}$$

The reaction mixture is submitted to steam distillation, when benzaldehyde passes over. The residual liquid is then treated with hydrochloric acid to precipitate benzoic acid.

Benzal chloride is also used for the preparation of cinnamic acid on a commercial scale.

13. **Benzene Hexachloride** (BHC).—When benzene is treated with excess of chlorine in the presence of sunlight, benzene hexachloride is produced. Four isomeric forms (α, γ, β and δ) of this compound have been obtained in a pure state so far. They must be regarded as *cis-trans* isomerides (having different positions of the chlorine atoms on the two sides of the plane of the carbon ring). The γ-isomer (formula in the margin), called lindane, is a powerful insecticide, and is produced in slightly greater amounts than DDT. It is particularly effective against ball weevil, leaf hopper and flea worm.



Lindane

QUESTIONS

1. Under what conditions can chlorine react with benzene ? What are the products formed and under what conditions the halogen can be removed from them ? (*Rajasthan, B.Sc., 1961; Ajmer, B.Sc., 1961*)

2. How does chlorine act upon toluene under different conditions ? Indicate how benzyl alcohol, benzaldehyde and benzoic acid are obtained from chlorination products of toluene. (*Madras, B.Sc., 1943*)

3. Write all the reactions between chlorine and toluene. What shall be the various compounds formed and how will they be detected ? (*Saugar, B.Sc., 1962*)

4. Discuss in detail, the several aspects of halogenation of toluene Name the somers having the formula C_7H_7Cl. How would you distinguish them ? (*Gorakhpur, B.Sc., 1962*)

5. An organic compound, A, was found to contain C=52·2, H=3·7, and Cl=41·4 per cent. When submitted to oxidation, it gave an acid *B* which on being distilled with soda-lime, yielded benzene. Deduce the identity of both *A* and *B*. [*Ans.* (*A*) Benzal chloride, $C_6H_5CHCl_2$ (*B*) Benzoic acid, C_6H_5COOH.]

6. A certain hydrocarbon, on being treated with chlorine under suitable conditions, gave three different products, *A*, *B* and *C* each containing 28·0 percent of chlorine. When submitted to oxidation with alkaline potassium permanganate *A*, *B* and *C*, each yielded a monobasic acid. The acid obtained from *A*, when distilled with soda lime, gave benzene, while those from *B* and *C*, on similar treatment, each yielded 1 chlorobenzene. Deduce the possible identity of *A*, *B* and *C*. [*Ans.* (*A*) Benzy chloride ; (*B*) and (*C*) *o*- and *p*-chlorotoluenes.]

7. A compound (*A*) contains C, 66·4% H, 5·53%, Cl, 28·07%. Upon reaction with caustic soda solution it yields a compound (*B*) containing C, 77·8%, H, 7·4% and O, 14·8%. Oxidation of (*A*) produces an acid (*C*) containing C, 68·85%, H, 4·92% and O, 26·23%. Give possible structures for the compound (*A*) and its isomers. (*Allahabad, B.Sc., 1950*)

Ans. (*A*) is benzyl chloride, $C_6H_5CH_2Cl$; its isomers are *o*-, *m*- and *p*-chlorotoluenes, $C_6H_4<\begin{smallmatrix}CH_3\\Cl\end{smallmatrix}$.

8. Mention conditions under which chlorine acts on toluene. Write down the formulae of various chloro compounds formed. How would they be generally distinguished from one another ? (*Rajasthan, B.Sc., 1960*)

9. Describe the common methods of preparing the aliphatic and aromatic halogen derivatives. Compare the chemical activity of ethyl chloride with that of chlorobenzene.

(*Bombay, B.Sc., Chemistry Subs., 1962*)

10. How will you distinguish between nuclear and side-chain chloroderivatives of toluene ? (*Bombay, B.Sc., Chemistry Subs., 1962*)

11. Describe the conditions under which nuclear and side-chain halogenation of an organic hydrocarbon is affected. Give an account of the general reactions of these two types of halogen derivatives and point out their differences.

(*Allahabad, B.Sc., 1961*)

CHAPTER FORTY-TWO

AROMATIC NITRO COMPOUNDS

1. Nitration. As already mentioned, a characteristic property of aromatic compounds is the ease with which they may be converted into nitro-compounds :

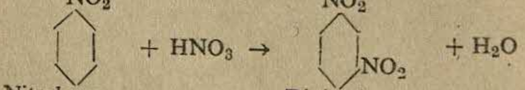
$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

The process, known as *nitration*, is of great practical importance. The actual details of the process depend on the nature of the compound to be nitrated and on the number of nitro-groups to be introduced.

2. General Methods of Nitration.—

(1) *By means of a Mixture of Concentrated Nitric and Sulphuric Acids.* The nitration of aromatic compounds is generally effected by means of concentrated nitric acid in the presence of concentrated sulphuric acid. The latter serves to "bind" the water produced in the reaction and thus to maintain the effective concentration of the former. It also diminishes the oxidizing action of nitric acid on the side-chain, if present.

If it is desired to introduce more than one nitro-group in the molecule of an aromatic hydrocarbon, an excess of a mixture of *fuming* nitric acid and concentrated sulphuric acid is employed. Thus, *m*-dinitrobenzene is prepared by heating a mixture of nitrobenzene, fuming nitric acid and concentrated sulphuric acid :



Nitrobenzene *m*-Dinitrobenzene

If a higher temperature and an excess of the nitrating acid mixture is used, di- and tri- nitro-derivatives are formed.

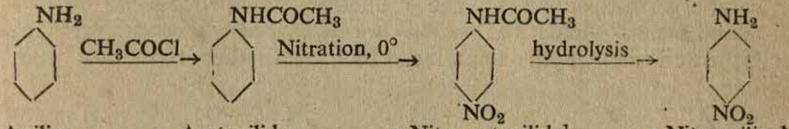
The nitration is facilitated by the presence in the nucleus of certain substituents, *e.g.*, the halogen, the hydroxyl and the alkyl groups.

(2) *By means of a Mixture of Concentrated Nitric acid and Acetic Anhydride* (**Pictet and Khotinsky's method**). This mixture is a very energetic nitrating agent, and gives better yields of nitro-compounds. The acetic anhydride, like sulphuric acid, serves to take up the water.

(3) *By means of Nitrogen Tetroxide in the presence of Anhydrous Aluminium Chloride* (**Schaarschmidt's method**). This method consists

in treating the substance to be nitrated with liquid or gaseous nitrogen tetroxide in the presence of anhydrous aluminium chloride, which acts as a catalyst.

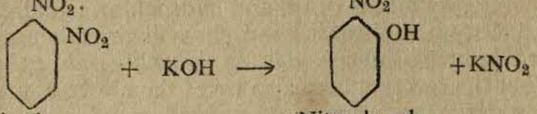
4. Nitration of Amino Compounds.—The nitration of an aromatic amino-derivative cannot be carried out directly, as the amino group is oxidized, and a tarry product is obtained. The method here followed consists in **protecting or blocking the amino group** by acetylation, nitrating the resulting derivative, and finally hydrolysing the $-NHCOCH_3$ group to regenerate the $-NH_2$ group :—



Aniline Acetanilide *p*-Nitroacetanilide[1] *p*-Nitroaniline[1]

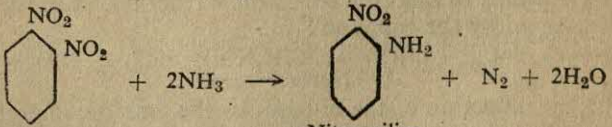
5. Physical Properties.—Nitro-compounds are oily liquids or crystalline solids, and are usually yellow in colour. They are practically insoluble in water, but readily dissolve in alcohol, ether and other organic solvents. Many of them can be distilled in steam.

6. Reactions.—(1) *Replacement of Nitro Group.* In the mono-substituted derivatives, the nitro-group is firmly united to the benzene ring, and cannot be directly replaced by other atoms or groups. However, in the case of polynitro-derivatives, or halogen-substituted nitro-compounds, the nitro group is more or less readily replaceable by other substituents. Thus, orthodinitro-benzene, when boiled with aqueous potash, yields ortho-nitrophenol,



o-Dinitrobenzene *o*-Nitrophenol

and with alcoholic ammonia, it gives *o*-nitroaniline :



o-Nitroaniline

(2) *Reduction of Nitro-Compounds.* This is the most important reaction of the nitro-compounds, and is discussed in the next section.

(3) *Explosive Nature of Polynitro-Compounds.* Polynitro-compounds, such as trinitrobenzene, trinitrotoluene (T.N.T.) and trinitrophenol, explode violently when detonated or suddenly heated. The last two compounds are extensively used as explosives.

7. Reduction of Nitro Compounds.—The behaviour of aromatic nitro-compounds on reduction is of great theoretical and practical importance. When the reduction is effected by purely chemical methods the *final products*, as in the case of aliphatic nitro-compounds, are amino-derivatives. Thus nitrobenzene yields aminobenzene (aniline) :

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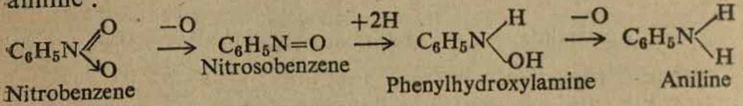
[1] *o*-Nitro-isomer is also formed.

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$

By carrying out the reaction under suitable conditions, it may be made to yield various *intermediate products.* The most important factor controlling the course of the reaction is the alkalinity or acidity of the medium.

Bamberger has shown that the reduction of nitrobenzene in **acid** or **neutral solution** yields the **mononuclear intermediate products**, nitrosobenzene and phenylhydroxylamine, which on further reduction give aniline :



Reduction in Neutral Solution.—

In the case of a *neutral* reducing agent, such as zinc-dust and water, nitrosobenzene is first produced, and is then converted into phenylhydroxylamine. When hydrogen is passed into an alcoholic solution of nitrobenzene containing colloidal palladium, aniline is obtained. Thus, in a neutral medium it is possible to get all the three products.

Reduction in Acid Solution.—

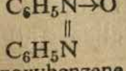
On the other hand, when the reduction is carried out in an *acid* solution. *e.g.*, by means of tin and hydrochloric acid, the intermediate products, nitrosobenzene and phenylhydroxylamine, do not at all appear, *the amino compound being the only product that can be isolated.* That the reaction here also takes the above course follows from the fact that the velocity of reduction of nitrobenzene by stannous chloride in the presence of a large exeess of hydrochloric acid corresponds to that of a *bimolecular* reaction. It must, therefore, be represented by the equation :

$$C_6H_5NO_2 + SnCl_2 + nHCl \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} + SnCl_4 + H_2O + (n-2)HCl$$

The further reduction of the nitroso- to the amino-compound is far more rapid ; hence the impossibility of isolation of the intermediate products.

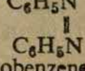
Reduction in Alkaline Solution.—

When reduction is carried out in alkaline solution, the above mononuclear products tend to interact with one another, yielding the more complex **dinuclear intermediate products**, azoxybenzene, azobenzene and hydrazobenzene :



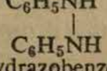
$$\begin{array}{c} C_6H_5N\rightarrow O \\ \| \\ C_6H_5N \end{array}$$

Azoxybenzene



$$\begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array}$$

Azobenzene



$$\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5NH \end{array}$$

Hydrazobenzene

Azoxybenzene has been shown to be produced by the condensation of nitrosobenzene with phenylhydroxylamine :

$$\begin{array}{c} C_6H_5NO \\ + \\ C_6H_5NHOH \end{array} \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5\overset{}{N}O \end{array} + H_2O,$$

and undergoes further reduction to *hydrazobenzene*,

$$\begin{array}{c} C_6H_5N \\ \| \\ C_6H_5NO \end{array} + 4H \longrightarrow C_6H_5NH.NH.C_6H_5 + H_2O$$

which then reacts with unchanged nitrobenzene, yielding *azobenzene* :

$$4C_6H_5NH.NH.C_6H_5 + 2C_6H_5NO_2 \longrightarrow 5C_6H_5N{=}NC_6H_5 + 4H_2O$$

Azobenzene is also produced directly from phenylhydroxylamine under the condensing action of alkali :

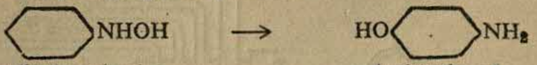
$$C_6H_5N<\begin{array}{l} H \\ OH \end{array} + \begin{array}{r} HO \\ H \end{array}>NC_6H_5 \longrightarrow C_6H_5N{=}NC_6H_5 + 2H_2O$$

8. Electrolytic Reduction.—The course of the electrolytic reduction of nitro-compounds has been studied by Haber (1898—1900). The *primary* products of electrolytic reduction in both acid and alkaline solutions are as before, *viz.*,

$$C_6H_5NO_2 \longrightarrow C_6H_5NO \longrightarrow C_6H_5NHOH \longrightarrow C_6H_5NH_2$$

These give rise to *secondary* or chemical reduction products.

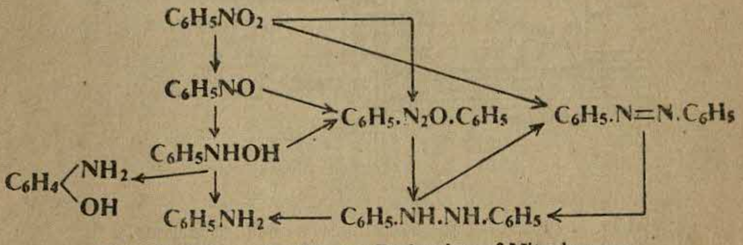
In weakly acid solution, with addition of alcohol to increase the solubility, nitrobenzene gives a good yield (about 90 per cent) of aniline. If, on the other hand, a strongly acid solution be employed, *p*-aminophenol is obtained as the main product, owing to the isomerization of phenylhydroxylamine :



Phenylhydroxylamine *p*-Aminophenol

In alkaline solution, on the other hand, nitrosobenzene and phenyl-hydroxylamine combine together as before, yielding azoxybenzene, which then undergoes further reduction to hydrazobenzene. The latter compound, in its turn, is reduced to aniline, small proportion of it being oxidized by nitrobenzene and atmospheric oxygen to azobenzene.

The behaviour of nitrobenzene on electrolytic reduction has been represented schematically by Haber as follows, the vertical



Haber's Scheme for Electro-Reduction of Nitrobenzene.

and horizontal arrows indicating the primary, and the oblique arrows secondary reactions.

9. **Nitrobenzene, $C_6H_5NO_2$.**—This compound is prepared by the nitration of benzene with mixed acid at about 50°C.

Expt. 1. Preparation of Nitrobenzene. To 50 ml. of pure benzene, placed in a half-litre flask, is added, in small quantities at a time, a well-cooled mixture of concentrated nitric acid (60 ml.) and concentrated sulphuric acid (70 ml.). After each addition, the contents of the flask must be well shaken and the flask cooled under the tap. The temperature must not be allowed to rise above 50° as this would result in the formation of dinitrobenzene. When all the acid mixture has been added, a vertical air condenser is attached to the flask which is then heated for about an hour by immersion in a water-bath kept at about 50°, the flask being well-shaken periodically during the heating.

After cooling, the contents of the flask are poured into a separating funnel and the *lower layer of acids* is run off.. The oily nitrobenzene is washed once with water, then with dilute sodium carbonate solution and finally again with water, the *lower layer of nitrobenzene* being drawn off each time.

The nitrobenzene, which is turbid because of its being moist, is then allowed to stand over fused calcium chloride, until it gets quite clear. It is then distilled from a distillation flask, provided with a thermometer and a long air condenser, the fraction passing at 204° to 207° being collected separately. The distillation must not be carried out to dryness since this might lead to an explosion.

Manufacture. The method employed in the manufacture of nitrobenzene is similar to that used in the laboratory. The usual amounts of the reactants employed in one operation are :

Benzene	500 gallons
Nitric acid	5,000 lb.
Sulphuric acid	6,000 lb.

A sketch of the nitrobenzene plant is given in Fig. 1. The benzene is placed in the cast iron nitrating pan provided with lead cooling coils and a central shaft carrying two spiral agitators. The acid mixture contained in the mixed-acid pan is run into the nitrating pan,

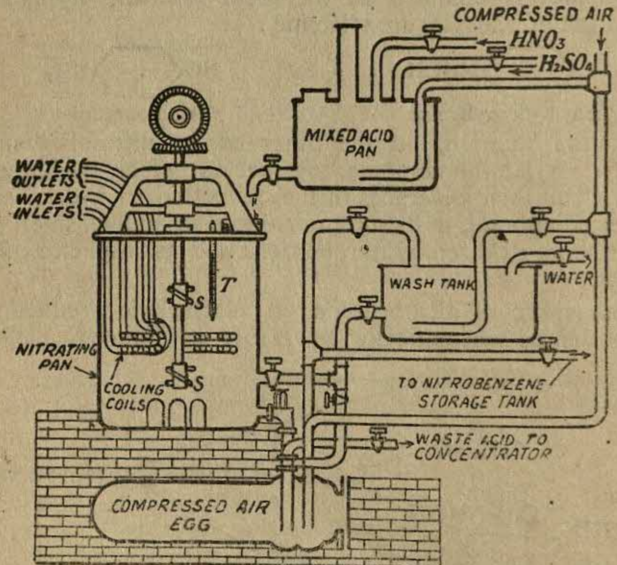


Fig. 1. Plant for the Manufacture of Nitrobenzene.

in a fine stream, the contents of the nitrating pan being constantly stirred. The flow of nitrating acid is so regulated that the temperature does not exceed 50°C. After the whole of the acid mixture has been added, the agitation of the nitrating pan is continued for 4½ hours. At the end of this time, the nitration is complete and the contents of the pan are allowed to settle for about five hours. The lower layer, consisting of dilute sulphuric acid, is run into the air-pressure egg, whence it is blown to a concentrator. The concentration of the acid is usually effected by the cascade system, and the concentrated acid is used once again.

When the waste acid has been forced into the concentrator, the nitrobenzene is run into the egg, and thence blown into the washing tank. Here it is mixed with an equal volume of water (containing a little sodium hydroxide to neutralize any free acid present), and the mixture is well agitated by means of a jet of compressed air. The contents of the washing tank are allowed to settle for several hours. The nitrobenzene, which now forms the lower layer, is run into the egg, and thence blown into storage tanks.

Properties. Nitrobenzene is a pale-yellow oil (*sp. gr.*, 1·2) at 20°, and has a strong odour like that of bitter almonds. It is insoluble in water, but dissolves in organic solvents. It boils at 209°C, and is volatile in steam.

When treated with tin and hydrochloric acid (or iron and water in the presence of a little hydrochloric acid), nitrobenzene is reduced to aniline :

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$

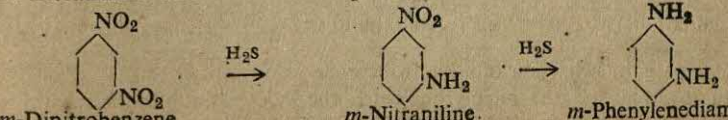
The reaction is of great commercial importance, since aniline is the starting material in the manufacture of dyes.

Uses. (1) The chief use of nitrobenzene is in the manufacture of aniline.

(2) It is also employed, under the name of **oil of mirbane,** in scenting cheap soaps, boot polishes, etc., where a disagreeable odour is to be covered.

10. ***m*-Dinitrobenzene,** $C_6H_4(NO_2)_2$.—This compound is prepared by gradually adding nitrobenzene (1 part) to a mixture of concentrated nitric acid (1½ parts) and concentrated sulphuric acid (3 parts). The reaction mixture is then heated on a steam bath (100°C), until a drop of the oily liquid, when stirred with cold water, solidifies completely. The product, while still hot, is poured into a large quantity of water. The solid *m*-dinitrobenzene that separates out is filtered, washed with cold water, and recrystallized from hot alcohol.

m-Dinitrobenzene forms pale-yellow crystals (*m.p.* 90°). When reduced with alcoholic ammonium sulphide, it is first converted into *m*-nitraniline and then into *m*-phenylenediamine :



m-Dinitrobenzene *m*-Nitraniline *m*-Phenylenediamine

Uses. *m*-Dinitrobenzene is employed for the preparation of *m*-nitraniline and *m*-phenylenediamine, both of which find application in the dye industry. It also enters into the composition of certain explosives.

11. *o*-**Dinitrobenzene** (*m.p.*, 118°) and *p*-**dinitrobenzene** (*m.p.*, 170°) are formed in small quantities during the preparation of *m*-dinitrobenzene. They resemble *m*-dinitrobenzene in their behaviour on reduction.

o-Dinitrobenzene *differs* from the other two isomerides in the fact that it reacts with boiling caustic alkalis, giving *o-nitrophenol* and, with hot alcoholic ammonia, yielding *o-nitraniline*.

12. **1,3,5-Trinitrobenzene** can be obtained as colourless crystals (*m.p.*, 121°) by heating benzene to 140°C with a mixture of nitric and fuming sulphuric acids. It is a useful military explosive.

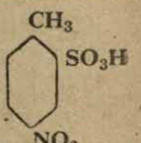
13. **Nitrohalogen Derivatives of Benzene**.—When the halogen derivatives of benzene are nitrated, they give only the *o*- and *p*-mononitro-derivatives. The *m*-nitro-halogen derivatives are obtained by chlorinating or brominating nitrobenzene. All the nitro-halogen derivatives are crystalline solids.

The *ortho*- and *para*-compounds differ[1] from the *meta*-compounds in being acted upon by alcoholic potash and by alcoholic ammonia at high temperatures, yielding the corresponding nitrophenols, $C_6H_4(OH)NO_2$, and nitranilines, $C_6H_4(NH_2)NO_2$.

14. **Nitrotoluenes,** $C_6H_4<\begin{smallmatrix}CH_3\\NO_2\end{smallmatrix}$.—When toluene is nitrated, it yields a mixture of *ortho*-and *para*-nitrotoluenes together with a small proportion of the *meta*-compound. The proportion of the *ortho*-derivatives is greater than that of the *para*-compound. The products are separated from the reaction mixture by a combination of fractional crystallization and fractional distillation.

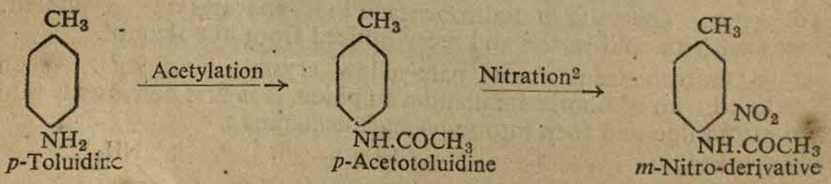
o-**Nitrotoluene** (*b.p.*, 218°) yields *o*-nitro-benzaldehyde on oxidation. It is largely used in the manufacture of *o*-toluidine, $C_6H_4(CH_3)NH_2$.

p-**Nitrotoluene** (*m.p.*, 53°, *b.p.*, 230°) is used in the manufacture of *p*-toluidine, $CH_3.C_6H_4.NH_2$. When treated with fuming sulphuric acid, it yields *p*-nitrotoluene-*o*-sulphonic acid (formula, in the margin) which is employed in the manufacture of the dye called Direct Yellow.



p-Nitrotoluene-*o*-sulphonic acid

m-**Nitrotoluene** (*m. p.* 16°, *b. p.* 230°) is best prepared from *p*-toluidine by an indirect method, shown below :—



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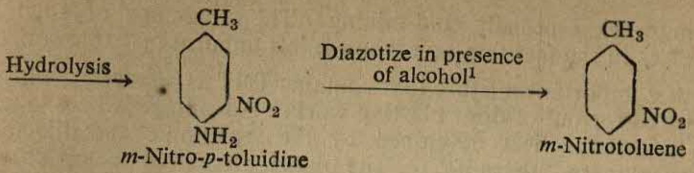
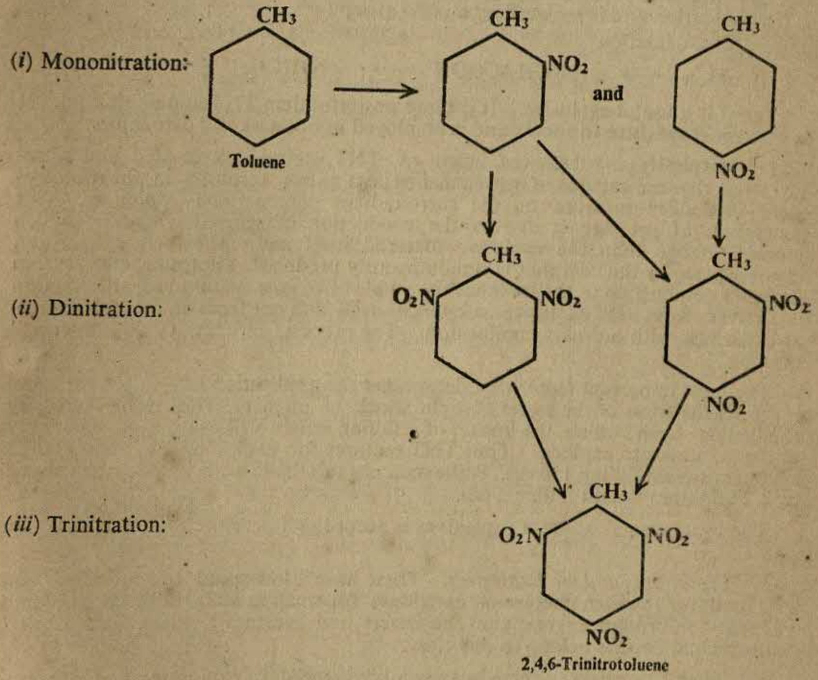
[1] Compare the behaviour of *o*-dinitrobenzene.

[2] In this reaction the nitro group enters the *ortho*-position to the substituted amino group, the para position being already occupied by the methyl group.



2,4,6-Trinitrotoluene (TNT).—This very important high explosive is prepared by nitration of toluene in three steps involving mononitration, dinitration and trinitration respectively. A mixture of nitric and sulphuric acids, to which a small proportion of *oleum* (that is sulphuric acid containing some SO_3) has been added to minimize the amount of water in the acid mixture, is used in bringing about nitration. The spent acid from trinitration is utilized for the dinitration and that from dinitration for the mononitration. The reactions taking place in all the three steps are summarized in the following scheme :—



Trinitrotoluene is a pale yellow, crystalline solid melting at 80·8°. It is a very important high explosive. A mixture of TNT (20 per cent) and ammonium nitrate (80 per cent), called **amatol**[2], is much employed in mining work, especially coal-mining. The advantage of such a mixture lies in the fact that no carbon is left unburnt on explosion.

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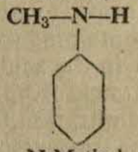
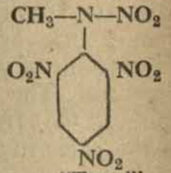
[1] The diazonium compound first produced is *reduced* by alcohol, the diazonium group being thereby replaced by hydrogen.

[2] Amatol=Ammonium nitrate+Trinitrotoluene.

Another important mixture that contains TNT is **ammonal**[1], which is employed for out-of-door blasting work. Advantage is here taken of the enormous heat developed by the oxidation of metallic aluminium (compare "thermite"). The usual percentage composition of ammonal is : Ammonium nitrate 47% ; aluminium 22% ; TNT 30% ; charcoal 1%.



N-Methyl-aniline



"Tetryl"

15. **N,2,4,6-Tetranitro-N-methylaniline,** commonly called "Tetryl."—This is an important explosive, and is a tetranitro derivative of methylaniline. It may be obtained from methylaniline, but is manufactured from the less expensive N,N-dimethylaniline by nitration with nitric acid in the presence of concentrated sulphuric acid. Three nitro groups enter the nucleus and one of the methyl groups suffers oxidation and is replaced by a nitro group :

$$-N(CH_3)_2 \xrightarrow{\text{oxidation}} -N(CH_3)COOH \xrightarrow{-CO_2} -NH(CH_3) \xrightarrow{\text{Nitration}} -N\!<^{NO_2}_{CH_3}$$

Tetryl is a useful explosive. It is more powerful than TNT and picric acid. It is also more sensitive to shock, and is employed in boosters and detonators.

16 **Explosives.**—Substances, such as TNT, tetryl, picric acid and nitroglycerine, that are capable of instantaneous combustion resulting in the development of sudden pressure on the surroundings are termed *explosives.* This generation of pressure is due to the production of gases having very much greater volume than the explosive material itself, and to the further expansion of these gases by the heat that is simultaneously produced. Explosion differs from ordinary combustion in the fact that the whole of oxygen required for the reaction is derived from the explosive substance itself and not from an external source, as is the case with ordinary combustion. The process, in fact, is an "internal" burning.

The most important factor that determines the application of a given explosive is the sensitiveness of the material to the shock of impact. This is measured by the height from which the impact of a falling weight will cause a small quantity of the substance to explode. Thus TNT requires for exploding an impact of 5 kilogram weight falling 150 cm., while mercury fulminate will explode when struck by a 2 kilogram weight falling 5 cm.

The usual classification of explosives is according to the use to which they are put; *e.g.*,—

(*i*) *Propellants or Low Explosives.* These have a low speed of explosion, and are used for the manufacture of cartridges for small arms (pistols, shotguns and rifles) and in ordnance (great guns, howitzers and mortars). Black gun-powder, ballistite and cordite belong to this class.

(*ii*) *High Explosives.* These possess a high speed of explosion and are employed for filling shells, bombs, mines and for demolitions. Nitroglycerine, TNT, tetryl and picric acid are examples of high explosives.

(*iii*) *Initiators or Detonators.* Some high explosives, especially those containing nitroglycerine, are capable of being fired directly. Others, *e.g.*, ammonal, require an explosive of a very sensitive type to initiate the explosion. This latter class of explosives are called initiators or detonators. Mercury fulminate and lead azide are the detonators that are commonly used.

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[1] Ammonal (Ammon for ammonium + al for aluminium).

17. Phenylnitromethane, $C_6H_5.CH_2NO_2$.—This is an example of a compound containing a nitro group in the sides-chain. It is prepared by heating benzyl iodide, $C_6H_5.CH_2I$, with silver nitrite (compare nitro-paraffins). Like other primary nitroparaffins, phenylnitromethane is a **pseudo acid** ; its two isomeric forms were isolated by Hantzsch in 1895.

QUESTIONS

1. Describe the preparation of nitrobenzene in the laboratory. How can the following compounds be prepared from it:—(*a*) aniline, (*b*) phenol, (*c*) iodobenzene? (*Andhra, B.Sc., 1942*)

2. Describe the reduction of nitrobenzene under different conditions. Give the structural formulae of the compounds formed. How would you prepare *m*-dinitrobenzene ? (*Allahabad, B.Sc., 1952*)

3. On combustion, 0.337 gm. of an organic compound, *A*, gave 0·561 gm. of CO_2 and 0·077 gm. of water. The compound contains 16·7 per cent of nitrogen. On reduction, it gave a derivative, *B*, having the following percentage composition: C=52·2, H=4·35, N=20·3, O=23·15. The compound, *B*, forms a hydrochloride containing 20.92 per cent of hydrochloric acid. Find the formula of *A* and *B*. (*Punjab, B.Sc., Hons. 1926*)

[*Ans:* $A = C_6H_4\,(NO_2)_2$; $B = C_6H_4(NO_2).\,NH_2$]

4. Write a short note on Reduction Products of Nitrobenzene. (*Lucknow, B.Sc., 1961*)

5. Describe the preparation of a pure sample of nitrobenzene in the laboratory. Explain with the aid of equations how nitrobenzene may be converted to *m*-nitraniline and azo-benzene. (*Venkateswara, B.Sc., 1960*)

6. Describe the preparation of nitrobenzene. How can the following be prepared from it ?

Aniline ; Phenol; and Chlorobenzene. (*Saugar, B.Sc., 1961*)

7. Describe the laboratory method of preparation of nitrobenzene. Give a brief account of the products obtained by its reduction under various conditions. (*Venkateswara, B Sc., 1961*)

8. Describe the preparation of nitrobenzene in the laboratory and give an account of the reactions which occur when nitrobenzene is reduced under different experimental conditions. (*Bihar, B.Sc., 1961*)

9. Describe the laboratory preparation of nitrobenzene. Starting from nitrobenzene, how would you prepare (*a*) aniline, (*b*) phenol, (*c*) phenylhydroxylamine and (*d*) *m*-dinitrobenzene. (*Gauhati, B.Sc., 1962*)

10. How is nitrobenzene obtained (*i*) in the laboratory, and (*ii*) on the large scale ?

Discuss the reduction of nitrobenzene under neutral, acidic and alkaline conditions. (*Punjab, B.Sc., 1962*)

AROMATIC AMINO COMPOUNDS

1. Classification.—The aromatic amino compounds are derived from ammonia in the same manner as the aliphatic amines. They are divided into **two main groups.** In the first group, which is by far the more important, the nitrogen is attached *directly* to the benzene nucleus, while in the second, it is present in the side-chain.

The members of the first group, *i.e.*, the true aromatic amino derivatives are divided into the following classes :—

(1) *Primary Aromatic Amino Compounds.*[1] These contain one or more amino-groups, $-NH_2$, linked directly to the benzene nucleus. They are called mono-, di-, tri-, etc., amino-compounds, according to the number of NH_2 groups that they contain, *e.g.*,

$C_6H_5NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$
Monoaminobenzene	Diaminobenzene	Triaminobenzene

(2) *Secondary Amines.* These are sub-divided into two groups :

(*i*) Purely aromatic secondary amines, *e.g.*, diphenylamine, $(C_6H_5)_2NH$.

(*ii*) Mixed aliphatic-aromatic secondary amines, *e.g.*, methylaniline, $C_6H_5.NHCH_3$.

(3) *Tertiary Amines.* These, like secondary amines, are divided into two groups : purely aromatic, *e.g.*, triphenylamine, $(C_6H_5)_3N$, and mixed aliphatic-aromatic, *e.g.*, dimethylaniline[2], $C_6H_5N(CH_3)_2$.

The second main group of the aromatic derivatives of ammonia consists of compounds containing the nitrogen atom in the *side-chain* of an alkylbenzene. Being substituted aliphatic amines, the members of this group closely resemble the aliphatic amines, in their chemical behaviour. They are, as usual, divided into three classes, *primary*, *secondary* and *tertiary*. The respective examples of three classes are :—Benzylamine, $C_6H_5CH_2NH_2$; Dibenzylamine, $(C_6H_5CH_2)_2NH$; Tribenzylamine, $(C_6H_5CH_2)_3N$.

1. PRIMARY AMINO COMPOUNDS

2. Methods of Formation.—

(1) **Reduction of nitro compounds.** The most important method of preparation of aromatic amino-compounds is by reduction of the corresponding nitro compounds :

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$

---

[1] The term "*amino compound*" rather than 'amine' is generally preferred, as these compounds differ in some important respects from the aliphatic amines.

[2] Or, more correctly, N,N-dimethylaniline.

The reduction is effected by various means, such as by the use of tin and hydrochloric acid, stannous chloride and hydrochloric acid, iron and hydrochloric acid, alcoholic ammonium sulphide, alcoholic stannous chloride, or electrolytically. Hydrogen in the presence of *Raney nickel catalyst* is also a very efficient reducing agent for aromatic nitro compounds.

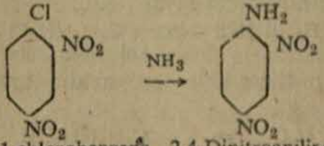
A general method of **reducing one nitro-group at a time** in the case of compounds containing two or more nitro groups in the molecule is by means of sulphides in alkaline solution. The laboratory method consists in suspending the polynitro compound in alcoholic ammonia, and passing in hydrogen sulphide. On the commercial scale, sodium sulphide is used.

(2) **From halogen compounds.** Aromatic halogen compounds are converted into amino-compounds when heated with aqueous ammonia at very high temperatures in autoclaves in the presence of a cuprous salt (catalyst). Thus, chlorobenzene is converted into aniline to the extent of 80 per cent under these conditions :

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2NH_3 \xrightarrow{\text{Cuprous salt, } 200^\circ} \underset{\text{Aniline}}{C_6H_5NH_2} + NH_4Cl$$

Because of the very high pressures developed at temperatures necessary for the reaction, and the consequent need for special equipment, the method is available for industrial use only.

Aromatic halogen derivatives containing one or more nitro-groups in the ortho- or *para*-positions with respect to the halogen atom are as reactive as alkyl halides. They react with ammonia (and also with amines) as readily as alkyl halides ; *e.g.*,



2,4-Dinitro-1-chlorobenzene 2,4-Dinitroaniline

(3) **From Phenols.** Aromatic amino-compounds can also be obtained from phenols by heating the latter at 300°C with the double compounds of zinc chloride and ammonia, $ZnCl_2.NH_3$, *e.g.*,

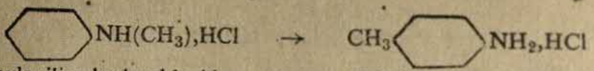
$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

(4) **From carboxylic acids.** Amino-compounds may also be obtained from aromatic acids having the carboxyl group in direct union with the benzene ring. The ammonium salt of the acid, when submitted to **Hofmann's bromamide reaction**, yields the amino-compounds. Thus :

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} \rightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

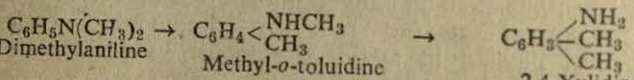
(5) **Isomerization of Alkylanilines.** A method of preparing the homologues of aniline was discovered by A. W. Hofmann, and is employed on a **commercial scale** in the dyestuff industry. The hydrochloride of a secondary or a tertiary mixed aliphatic-aromatic amine, or a quaternary ammonium salt, is heated to 300°C, in a closed

vessel, when the alkyl group migrates from the side-chain to the nucleus. Thus, methylaniline hydrochloride yields *p*-toluidine hydrochloride[1] :



Methylaniline hydrochloride → *p*-Toluidine hydrochloride

Similarly, dimethylaniline gives 2,4-xylidine, the change taking place in two stages :



$$C_6H_5N(CH_3)_2 \rightarrow C_6H_4{<}\begin{matrix}NHCH_3\\CH_3\end{matrix} \rightarrow C_6H_3\begin{matrix}NH_2\\CH_3\\CH_3\end{matrix}$$

Dimethylaniline — Methyl-*o*-toluidine — 2,4-Xylidine

This reaction is employed for preparing, on commercial scale, the higher homologues of aniline from aniline, toluidine, etc., because these latter can be readily converted into alkylanilines, alkyltoluidines, etc., which are then submitted to the above treatment.

3. Physical Properties.—Aromatic primary amino-compounds possess a characteristic but not objectionable odour. They are colourless liquids or solids. On exposure to air and light, they darken in colour. They are sparingly soluble in water, are volatile in steam, and can be distilled without decomposition under the atmospheric pressure.

4. Reactions of Aromatic Amino Compounds.—

(1) Basic nature. On account of the electronegative character of the benzene nucleus, aromatic amino-compounds are considerably weaker bases than aliphatic amines. They are neutral towards litmus, but form stable salts with mineral acids ; *e.g.*,

$$\underset{\text{aniline}}{C_6H_5NH_2} + HCl \longrightarrow \underset{\text{Anilinium chloride}}{C_6H_5NH_3Cl}$$

The aqueous solutions of these salts are acidic towards litmus on account of hydrolysis ; *e.g.*,

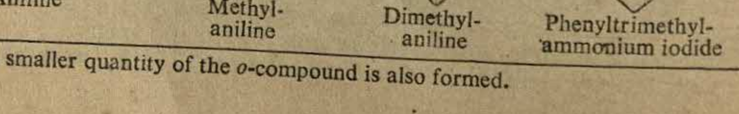
$$C_6H_5NH_3Cl + H_2O \rightleftharpoons \underset{\text{Anilinium hydroxide}}{C_6H_5NH_3OH} + HCl$$

When an aromatic amino compound is added to an aqueous solution of a heavy metal salt, the heavy metal hydroxide is precipitated ; *e.g.*,

$$FeCl_3 + 3C_6H_5NH_3OH \rightleftharpoons Fe(OH)_3 + 3C_6H_5NH_3Cl$$

This is a conclusive proof of the existence of an **aryl-substituted ammonium hydroxide** in aqueous solution.

(2) Alkylation. Like aliphatic amines, aromatic amino-compounds can be alkylated right up to the quaternary ammonium salts ; *e.g.*,



Aniline — Methyl-aniline — Dimethyl-aniline — Phenyltrimethyl-ammonium iodide

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[1] A smaller quantity of the *o*-compound is also formed.

The secondary alphyl-aryl amines are stronger bases than the primary aromatic amino-compounds ; the tertiary compounds are still stronger. The quaternary ammonium bases, *e.g.*, $[C_6H_5N(CH_3)_3]OH$, possess, as usual, a strongly alkaline reaction.

(3) **Acylation.** Aromatic amino-compounds are readily acylated, *i.e.*, the hydrogen of the NH_2 group can be replaced by various acid radicals. The aryl-substituted acid amides, thus obtained, are called **anilides.** Acylation can be effected by heating the amino-compounds with anhydrous acid, or better by treating them with acid chlorides or anhydrides in the cold, *e.g.*,

$$C_6H_5NH_2 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \rightarrow \underset{\text{Acetanilide}}{C_6H_5NH.COCH_3} + CH_3COOH$$

The most efficient method of benzoylation of aromatic amino-compounds is that of **Schotten-Baumann.** In this method the compound to be benzoylated is shaken with an excess of benzoyl chloride and dilute sodium hydroxide solution:

$$C_6H_5NH_2 + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\text{Benzanilide}}{C_6H_5NH.COC_6H_5} + HCl$$

As in the case of aliphatic amines, acylation completely obliterates the basic character of aromatic amino-compounds. The anilides, therefore, are *neutral* compounds, no more soluble in dilute hydrochloric acid than in water.

(4) **Carbylamine reaction.** Like aliphatic primary amines, aromatic amino-compounds react with chloroform and alcoholic potash, yielding highly obnoxious smelling carbylamines : *e.g.*,

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl carbylamine}}{C_6H_5NC} + 3KCl + 3H_2O$$

(5) **Condensation with aromatic aldehydes.** Aromatic amino compounds undergo condensation with aromatic aldehydes, yielding **anil derivatives** (*Schiff's bases*) of the aldehydes :

$$\underset{\text{Aniline}}{C_6H_5N}\boxed{H_2 + O}\underset{\text{Benzaldehyde}}{=CHC_6H_5} \rightarrow \underset{\text{N-Benzalaniline}}{C_6H_5N=CHC_6H_5} + H_2O$$

(6) **Diazo reaction.** The most important reaction of aromatic amino-compounds, which distinguishes them from aliphatic primary amines, is that when treated with nitrous acid at *low temperature* (0°C) and in the presence of excess hydrochloric (or sulphuric) acid, they form diazonium salts, which are of great practical importance (see next chapter) :

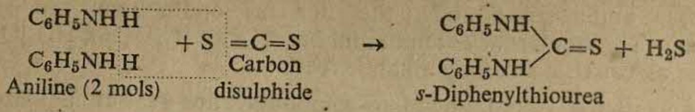
$$\underset{\text{Aniline}}{C_6H_5NH_2} + HNO_2 + HCl \rightarrow \underset{\substack{\text{Benzene-}\\\text{diazonium chloride}}}{C_6H_5N_2Cl} + 2H_2O$$

If the reaction mixture be *warmed*, the diazonium compound is hydrolysed with evolution of nitrogen and the production of a phenol:

$$C_6H_5N_2Cl + HOH \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + HCl + N_2$$

(7) **Reaction with carbon disulphide.** When an aromatic amino-compound is heated with carbon disulphide in the presence of powdered potassium hydroxide as catalyst, we get a symmetrical

diaryl-substituted thiourea; *e.g.*,



$$\begin{array}{l} C_6H_5NH\,H \\ C_6H_5NH\,H \end{array} + S{=}C{=}S \rightarrow \begin{array}{l} C_6H_5NH \\ C_6H_5NH \end{array}\!\!\!>C{=}S + H_2S$$

5. **Aniline,** *Aminobenzene* or *Phenylamine*, $C_6H_5.NH_2$.—This is the simplest and the most important representative of the aromatic amino compounds containing the NH_2 group in direct union with the benzene nucleus. It is prepared in the laboratory by the reduction of nitrobenzene with tin and hydrochloric acid.

Nitrobenzene (40 gm.) and granulated tin (80 gm.) are placed in a 2-litre round bottom flask, fitted with a long vertical air-condenser. 200 ml. of concentrated hydrochloric acid are gradually added (about 10 ml. at a time) through the top of the condenser. The flask is shaken well after each addition. If the liquid begins to boil, the flask must be cooled under the tap to avoid loss of nitrobenzene and aniline. Towards the end, the reaction becomes comparatively slow ; the remaining acid may then be added more quickly. To ensure complete reduction of nitrobenzene, the flask is heated on a water bath, until all the oily drops of nitrobenzene and its odour have disappeared.

To liberate the base from the solution containing the stannichloride $(C_6H_5NH_3)_2SnCl_6$, a solution of sodium hydroxide (160 gm. in 230 ml. of water) is *gradually* added. If during the addition of caustic soda the liquid begins to boil, it must be cooled under the tap. The addition of sodium hydroxide is continued until the stannic hydroxide, first precipitated, goes completely into solution, and the mixture shows strongly alkaline reaction.

The aniline separates out during the above process as a dark oil, and is recovered from the mixture by steam-distillation. The distillate consists of two layers : (*i*) a lower oily layer of aniline, and (*ii*) an upper aqueous layer containing aniline in solution and in suspension. The whole of it is saturated with common salt, and then extracted thrice with ether in a separating funnel using about 50 ml. of ether for each extraction. The ethereal solution is dehydrated over solid potassium hydroxide[1], and then the ether is distilled off. The residual aniline is now distilled, using an air condenser, and the fraction boiling at 180° to 185° is collected.

Manufacture. Aniline is prepared on a commercial scale by two different processes:—

(1) **From Nitrobenzene.** In this process nitrobenzene is reduced with iron and water in the presence of a small proportion of hydrochloric acid (catalyst):

$$C_6H_5NO_2 + 2Fe + 4H_2O \xrightarrow{HCl} C_6H_5NH_2 + 2Fe(OH)_3$$

The usual amounts of the reactants employed in one operation are:

Nitrobenzene, 1,000 lb.
Iron borings, 1,000 lb.
Water, 6 gallons.
Concentrated hydrochloric acid, 10 gallons.

The sketch of the aniline plant is given in Fig.1. The reduction pan is made of cast-iron, and has at its lower part a replaceable stone lining. This not only protects the vessel from the corrosive effect of the acid but also allows for wear due to the grinding action of the iron borings. The pan is provided with—

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[1] Calcium chloride cannot be used, as it forms a solid compound with amines just as it does with ammonia.

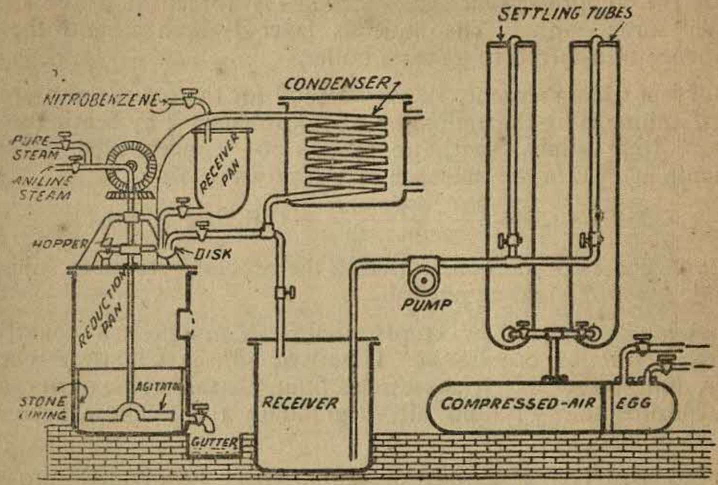


Fig. 1. Plant for the manufacture of Aniline.

(*i*) a hollow stirrer with two agitator blades and serving as an inlet for steam;

(*ii*) a still-head connected to a condenser.

(*iii*) a hopper, normally closed by means of a wooden plug, for introducing iron borings;

(*iv*) a dish connected through a stop-cock with the interior of the reduction pan.

Concentrated hydrochloric acid, water and about one-tenth of the iron borings are placed in the reduction pan, the remaining nine-tenths of iron borings are placed in the hopper, while the full charge of nitrobenzene is put into the nitrobenzene tank, placed at a higher level than the reduction pan. Steam, generated from water containing aniline in solution, is admitted into the reduction pan and the nitrobenzene is run in through the dish in a fine stream. A vigorous reaction sets in and nitrobenzene, aniline and water are carried over, in the form of vapour, to the condenser and from there flow back through the dish, into the reduction pan. After about one-tenth of nitrobenzene has been added, 100 lb. more of the iron borings are admitted by temporarily loosening the wooden plug of the hopper. The addition of nitrobenzene takes about 10 hours, during which time the full charge of iron borings is also added periodically as explained above. When the liquid returning from the condenser is colourless (indicating the absence of nitrobenzene), it is diverted to the receiving tank. The distillation takes about seven hours for its completion, pure steam, instead of that generated from aniline solution, being employed during the last hour. The distillate, which consists of water and aniline, is pumped into settling tubes, where it is allowed to stand for 48 hours. The lower layer of aniline is run off into the compressed-air egg, whence it is forced into the crude aniline storage-tanks. The aqueous layer is then run into the egg and thence transferred to a steam boiler.

(2) **From Chlorobenzene.** A new method for the industrial preparation of aniline is by the amination of chlorobenzene by heating under pressure (600 atmos.) with an excess of concentrated aqueous ammonia at 200° in the presence of a cuprous catalyst :

$$C_6H_5Cl + 2NH_3 \xrightarrow[\text{cuprous salt}]{200^\circ,\ 600\ \text{atmos.}} C_6H_5NH_2 + NH_4Cl$$

The large excess of ammonia, used in the process, serves to suppress the side reaction yielding phenol.

Physical Properties. When prepared fresh, aniline is a colourless, strongly refractive, oily liquid. It boils at 84°, is slightly soluble in water, and poisonous. It possesses a faint, characteristic odour, and, on exposure to light and air, it gradually turns yellow, becoming ultimately black.

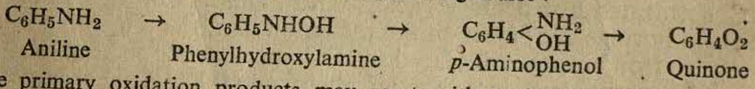
Reactions. The reactions of aniline may be divided into two groups :—

(1) **Reactions of the NH_2 group.** (See sec. 4, page 600.)

(2) **Behaviour on oxidation.** Aniline is very sensitive towards oxidizing agents, several products being formed according to the experimental conditions. The primary action is the reverse of what occurs in the reduction of nitrobenzene (chap. 42, sec. 7, page 589) :

$$\underset{\text{Aniline}}{C_6H_5NH_2} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5N{=}O} \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2}$$

These intermediate primary products then give rise to secondary products. Thus by oxidizing aniline by means of chromic acid, quinone is ultimately produced. The change may be supposed to take the following course :



$$\underset{\text{Aniline}}{C_6H_5NH_2} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \rightarrow \underset{p\text{-Aminophenol}}{C_6H_4{<}\begin{smallmatrix}NH_2\\OH\end{smallmatrix}} \rightarrow \underset{\text{Quinone}}{C_6H_4O_2}$$

The primary oxidation products may react with unchanged aniline or among themselves yielding *dinuclear* and *polynuclear* products. Thus, oxidation by means of alkaline permanganate yields azobenzene which is produced by the condensation of the intermediate product nitrosobenzene and unchanged aniline :

$$\underset{\text{Nitrosobenzene}}{C_6H_5.N\underline{O + H_2}} \underset{\text{Aniline}}{NC_6H_5} \rightarrow \underset{\text{Azobenzene}}{C_6H_5N{=}NC_6H_5} + H_2O$$

Similarly, oxidation with arsenic acid yields **violaniline**, a violet coloured substance. Potassium dichromate produces **aniline black**, which has been shown to be a mixture of several quinonoid substances. Bleaching powder imparts a temporary violet colour to aniline solution ; the reaction constitutes an exceedingly sensitive test for aniline.

(3) **Reactions of benzene nucleus.** The substitution of the amino-group for hydrogen of the nucleus makes the remaining hydrogen atoms readily replaceable by substituents. Thus, while benzene is only slowly attacked by bromine at the ordinary temperature, aniline is converted by bromine water into *s*-**tribromoaniline**. Again,

while benzene does not react with iodine except in the presence of oxidizing agents, aniline readily yields **mono-iodoaniline**, $C_6H_4I(NH_2)$. Nitric acid acts on aniline, producing resinous products.

Expt. 1. *~~Test of~~ Aniline* :—

(1) *Carbylamine Reaction.* (Chap. 12, sec. 14, reac. 3, p. 203).

(2) *Diazo Reaction.* If to some well-cooled solution of aniline, in dilute hydrochloric acid we add gradually a solution of sodium nitrite, we get a solution of benzene diazonium chloride. On warming a portion of this solution, nitrogen is evolved and the liquid develops the characteristic **odour of carbolic acid.** If to a second portion of the diazotized solution, a few drops of an alkaline solution of β-naphthol be added, a **scarlet-red precipitate** of an azo-dye is formed.

(3) *Bromination.* If bromine water be added to an aqueous solution of aniline, a **pinkish precipitate** of tribromaniline is formed, which soon turns grey-green.

(4) *Hypochlorite Test.* If a solution of sodium hypochlorite (or of bleaching powder) be added to an aqueous solution of aniline a **transient purple violet coloration** is developed.

(5) *Formation of Aniline-black.* If a few drops of potassium dichromate solution be added to a solution of aniline in dilute sulphuric acid a deep-blue or black colour is produced, owing to the formation of **"aniline-black."**

Uses. Aniline is one of the compounds of greatest practical importance. It is used in the manufacture of dyes and a very large number of other benzene derivatives.

6. Acetanilide, $C_6H_5NHCOCH_3$.—This important derivative of aniline is prepared by heating aniline with glacial acetic acid :

$$C_6H_5NH\vdots H + HO\vdots COCH_3 \rightleftharpoons C_6H_5NHCOCH_3 + H_2O$$

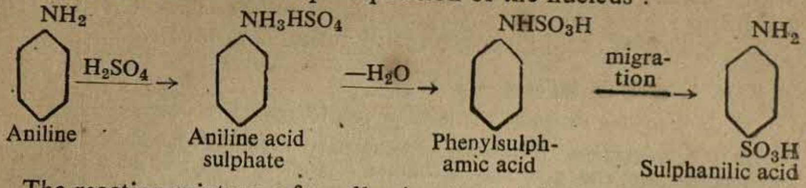
A mixture of equal weights of pure aniline and glacial acetic acid, together with about 3 per cent of anhydrous zinc chloride is gently boiled for about 3 hours in a flask fitted with a vertical air condenser. The reaction mixture, while still hot, is poured into a large quantity of cold water, and the precipitated acetanilide is filtered, and washed with cold water. It is then dissolved in boiling water, a little animal charcoal is added to the solution, which is then filtered at the boiling point. On allowing the filtrate to cool, acetanilide comes out in shining colourless plates.

Acetanilide crystallises in glistening plates (*m.p.*, 112°). It is sparingly soluble in cold water, but is **readily soluble in hot water.**

Dilute acids and alkalis hydrolyse acetanilide, producing aniline and acetic acid. Acetanilide is employed in medicine, under the name of **antifebrin**, for lowering the body temperature during fever.

7. Benzanilide, $C_6H_5NHCOC_6H_5$.—This compound is prepared from aniline by the **Schotten-Baumann process of benzoylation** (sec. 4, reac. 3, p. 601). It forms colourless, glistening plates (*m.p.*, 161°—162°).

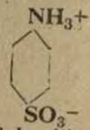
8. Sulphanilic Acid, *Aniline p-sulphonic Acid.*—This acid is prepared on a commercial scale by mixing equimolecular quantities of aniline and concentrated sulphuric acid. The resulting aniline acid sulphate is heated at 180°, until a test portion, on neutralization with sodium hydroxide, liberates no aniline. The latter reaction involves dehydration, followed by the migration of the sulphonic acid group from the side-chain to the para-position of the nucleus :



The reaction mixture, after allowing to cool, is poured into water, when sulphanilic acid dihydrate crystallizes out.

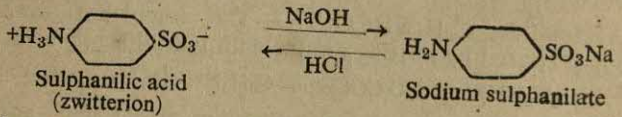
Properties. (1) *Zwitterion Structure.* The properties of sulphanilic acid are strikingly different from those of aromatic amino compounds and sulphonic acids. It is a crystalline, non-volatile solid that melts *with decomposition* at about 288°, and is insoluble in organic solvents.

It is sparingly soluble in cold water, readily so in hot water. These properties indicate that sulphaniline acid possesses the **zwitterion structure** shown in the margin (compare chap. 31, sec. 4, p. 462).



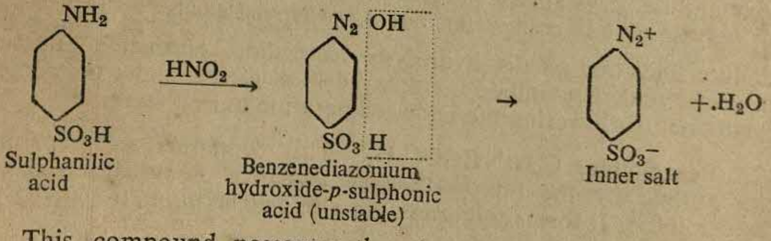
Sulphanilic acid (zwitterion)

(2) *Absence of Basic Properties.* Sulphanilic acid dissolves in alkalis but not in acids, showing complete suppression of basic properties :



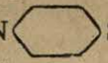
For the same reason, sodium salt, but not the free acid, can be acetylated.

(3) *Diazotization.* When a cold solution of sulphanilic acid in sodium hydroxide; mixed with a slight excess of sodium nitrite, is poured into well-cooled, dilute sulphuric acid, an *inner salt of benzene-diazonium hydroxide-p-sulphonic acid* is precipitated as colourless crystals :

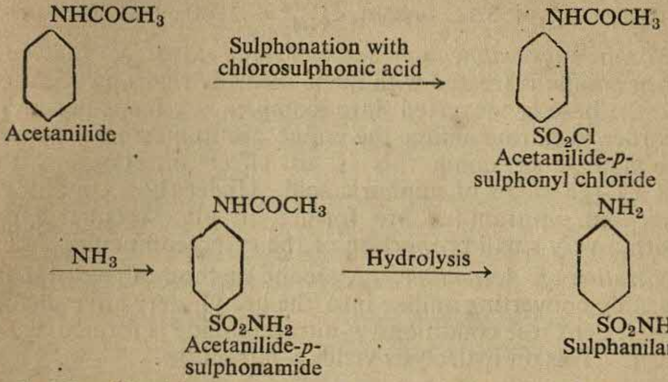


This compound possesses the characteristic properties of diazonium salts, and undergoes the usual coupling reactions with amines and phenols.

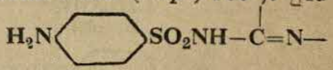
Uses. Sulphanilic acid is extensively used as an intermediate for **azo dyes.** It is also of great interest as the parent compound of the **sulpha drugs.**

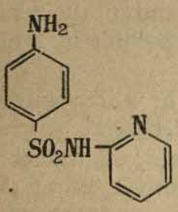
9. Sulphanilamide, *Aniline-p-sulphonamide,* H_2NSO_2NH_2.

The amide of sulphanilic acid is a valuable remedy against **streptococcal infections,** and is manufactured from acetanilide through the following steps[1] :—

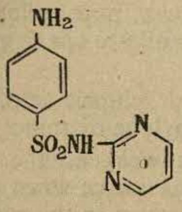

NHCOCH3
Acetanilide
Sulphonation with chlorosulphonic acid
NHCOCH3
SO2Cl
Acetanilide-p-sulphonyl chloride
NH3
NHCOCH3
SO2NH2
Acetanilide-p-sulphonamide
Hydrolysis
NH2
SO2NH2
Sulphanilamide

Sulphanilamide is a colourless, crystalline solid (*m.p.*, 166°). It is the parent compound of a family of well-known remedies that are collectively called **sulpha drugs.** They all posses the general formula given in the margin. A few examples are given below :—

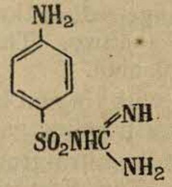




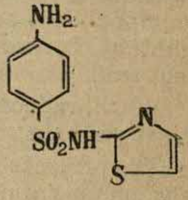
Sulphapyridine



Sulphadiazine

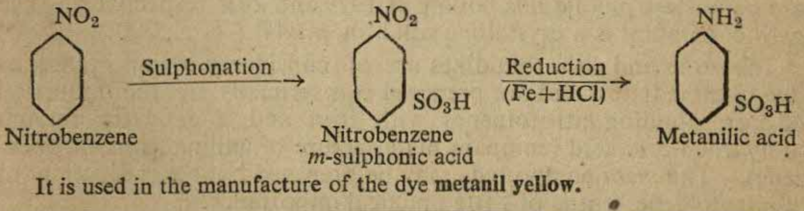


Sulphaguanidine



Sulphathiazole

10. Metanilic acid or *aniline-m-sulphonic acid*, is obtained from nitrobenzene as follows :



It is used in the manufacture of the dye **metanil yellow.**

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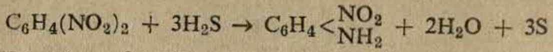
[1] Virtually, the synthesis involves sulphonation and amidation of aniline itself which, beforehand, is "protected" by acetylation, as in nitration. The final product is "deacetylated by hydrolysis."

11. Nitranilines. $C_6H_4(NH_2)NO_2$.

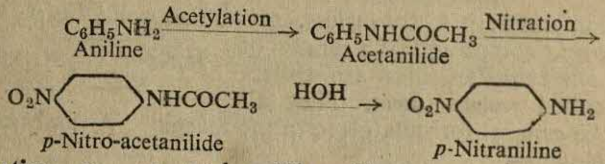
Preparation. (1) *By Partial Reduction of Dinitrobenzenes.*—The three nitranilines can be obtained by the *partial* reduction of the corresponding dinitrobenzenes by means of ammonium sulphide, as described below in the case of *m*-nitraniline :



$$C_6H_4(NO_2)_2 + 3H_2S \rightarrow C_6H_4{<}\begin{smallmatrix}NO_2\\NH_2\end{smallmatrix} + 2H_2O + 3S$$

(2) *By Nitration of Aniline in presence of large excess of Sulphuric Acid.* When aniline is treated with nitric acid, a vigorous reaction sets in, and the base is converted into complex, resinous products. Hence, in order to nitrate aniline the amino group must be "protected". One method of doing this is to effect nitration in the presence of a large excess of sulphuric acid. Under these conditions, *m*-nitraniline and *p*-nitraniline are formed in almost equal ratio, together with a very small proportion of the ortho-compound.

(3) *By Nitration of Acetanilide.* A second method of protecting the amino-group is by converting aniline into the acetyl derivative before nitration. Under these conditions, *p*-nitracetanilide is formed as the chief product. This on hydrolysis yields *p*-nitraniline.



Properties. *o*-, *m*- and *p*-Nitranilines are crystalline solids, melting at 71°, 114° and 147° respectively. The colour of the *ortho*-compounds is orange-red, of the *para*, pure yellow and of the *meta*-, midway between the two. They all are sparingly soluble in water, but readily so in alcohol.

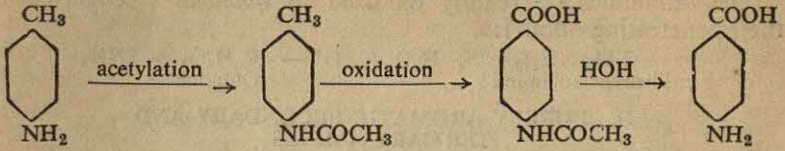
When, reduced with tin and hydrochloric acid, the three nitranilines yield the corresponding phenylene-diamines $C_6H_4(NH_2)_2$.

The presence of the nitro-group weakens the basic character of the amino-group. The effect is maximum when the NO_2 group is in the ortho position, somewhat less when in the para-, and the minimum when in the meta-position.

12. Toluidines, *Aminotoluenes.*—The *ortho* and *meta* toluidines are colourless oily liquids boiling at 197° and 203° respectively. The *para* compound is a crystalline solid (*m. p.*, 44° ; *b. p.*, 200°).

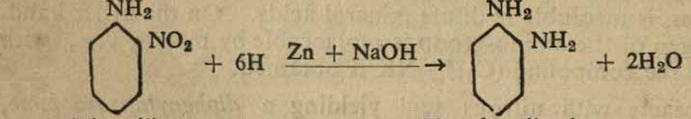
The *ortho* and *para* toluidines are of considerable importance as dye intermediates, and are prepared commercially by the reduction of corresponding nitrotoluenes with iron and a catalytic amount of hydrochloric acid (compare manufacture of aniline from nitrobenzene). The *meta* compounds may be prepared by the reduction of *m*-nitrotoluene, but is of little practical importance.

The three toluidines resemble aniline in chemical properties. Like aniline, they are very susceptible to oxidation and must be "protected" by acetylation before they can be nitrated or the side-chain oxidized. Thus, the conversion of a toluidine into the corresponding aminobenzoic acid is carried out through the following steps (compare preparation of *p*-nitraniline and of sulphanilamide) :—



13. **Diamino Compounds** or **Diamines.**—The diamino derivatives of benzene hydrocarbons are obtained by the reduction of dinitro- or aminoazo compounds. They are colourless solids more readily soluble in water, and less volatile, than monamino-compounds. They are strong bases, and their certain chemical properties differ according to the position of the amino-groups, as exemplified below in the case of the three diaminobenzenes.

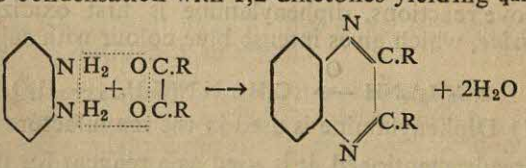
14. **Diaminobenzenes** or **Phenylenediamines.** $C_6H_4(NH_2)_2$.—The *o*-, *m*- and *p*- phenylenediamines are prepared by the reduction of the corresponding nitranilines; *e.g.*,



o-Nitraniline *o*-Phenylenediamine

o-, *m*-, and *p*- Phenylenediamines are crystalline solids, melting respectively at 102°, 63° and 147°. They are strong bases, and possess the typical characters of aromatic amino-compounds. The *m*- and *p*-compounds are very extensively used in the manufacture of dyes.

The three diaminobenzenes, in common with other diamines, possess certain properties which depend upon the relative positions of the two amino groups. The ortho-diamines, from the proximity of the two amino-groups, are characterised by the ease with which they undergo condensation with 1,2-diketones yielding **quinoxalines** :



The reaction occurs in the presence of acetic acid, the products obtained being yellow crystalline substances. It constitutes an **important test for *o*-diamines and for 1,2-diketones.**

The *m*-diamines are characterized by their reaction with nitrous acid, whereby brown dyes —**aminoazo compounds**— are produced by the condensation of two or more molecules of the diamine. Thus, *m*-phenylenediamine yields **Bismarck brown.** A solution of *m*-phenylenediamine in hydrochloric acid, on this account, is a useful reagent, and is employed in water analysis; in the presence of a trace of nitrite in water it acquires a yellow or orange coloration.

The *p*-diamines are readily oxidized to *quinones* (recognised by their penetrating odour):

$$\underset{p\text{-Phenylenediamine}}{C_6H_4(NH_2)_2} + H_2O + O \rightarrow \underset{\text{Quinone}}{C_6H_4O_2} + 2NH_3$$

II. PURELY AROMATIC SECONDARY AND TERTIARY AMINES

15. Diphenylamine, $(C_6H_5)_2NH$.—Diphenylamine is prepared by heating aniline hydrochloride with aniline at about 240° in a closed vessel.[1]

$$C_6H_5.NH_3Cl + H_2NC_6H_5 \rightarrow C_6H_5NHC_6H_5 + NH_4Cl$$

Properties. (1) Diphenylamine is a colourless crystalline substance (*m. p.* 54°; *b. p.* 310°), having an agreeable, floral odour. It is insoluble in water.

(2) Owing to the presence of two electronegative phenyl groups in its molecule, diphenylamine is only a feeble base, and its salts are decomposed by water. On this account, diphenylamine, unlike most bases, is insoluble in dilute mineral acids. On the other hand, the hydrogen of the amino-group is replaceable by metals, *e.g.*, with potassium the compound $(C_6H_5)_2NK$ is obtained.

(3) It reacts with nitrous acid yielding a *diphenylnitrosoamine*, $(C_6H_5)_2N.NO$, which is a yellowish-red oil (compare aliphatic secondary amines).

(4) A characteristic reaction of diphenylamine is with nitric and nitrous acids in the presence of concentrated sulphuric acid, an intense blue colour being developed in each case. The reaction is used for the identification of nitrates and sometimes also of nitrites.

Expt 2. Dissolve a crystal of diphenylamine in 3 or 4 ml. of concentrated sulphuric acid, add a drop of sodium nitrate solution; intense blue coloration is developed.

Add a drop of dilute solution of sodium nitrite to diphenylamine dissolved in concentrated sulphuric acid; blue coloration is produced.

In the above reactions, diphenylamine is first oxidized to *tetraphenylhydrazine*, which gives intense blue colour with sulphuric acid:

$$2(C_6H_5)_2NH \xrightarrow{O} (C_6H_5)_2N.N(C_6H_5)_2 + H_2O$$

Uses. (1) Diphenylamine is used in the manufacture of dyes.

(2) As already mentioned, it is used as a reagent for the detection of nitrates and nitrites.

(3) It is also employed in experiments requiring a constant high temperature, as for instance in the Victor Meyer method of molecular weight determination.

16. Triphenylamine, $(C_6H_5)_3N$.—This compound may be obtained by heating potassium diphenylamine with bromobenzene at 300°:

---

[1] Similarly other purely aromatic secondary amines are obtained by heating mixtures of primary amino-compounds and their hydrochlorides.

$$(C_6H_5)_2N\boxed{K + Br}C_6H_5 \longrightarrow (C_6H_5)_3N + KBr$$

Triphenylamine is a colourless, crystalline solid (*m.p.* 127°). It has no basic properties whatever[1], and does not combine with acids; nor does it react with nitrous acid[2].

III. ALIPHATIC-AROMATIC SECONDARY AND TERTIARY AMINES AND QUATERNARY AMMONIUM BASES

17. The compounds derived from the aromatic primary amino-compounds by the replacement of one or both of the hydrogen atoms of the NH_2 group by alkyl radicals are of great importance, and are usually called **alkylanilines.** The methods employed for their preparation and their chief properties are exemplified in the two methylanilines described below.

18. Methylaniline, $C_6H_5NH(CH_3)$.—This compound is obtained from pure aniline in the following steps:

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{\text{Glacial acetic acid}} \underset{\text{Acetanilide}}{C_6H_5.NH.COCH_3} \xrightarrow{Na} \underset{\text{Sodium acetanilide}}{C_6H_5.NNa.COCH_3}$$

$$\xrightarrow{CH_3I} \underset{\text{N-Methylacetanilide}}{C_6H_5.N(CH_3).COCH_3} \xrightarrow{\text{KOH (aq.)}} \underset{\text{Methylaniline}}{C_6H_5.NH.CH_3}$$

Methylaniline is a colourless liquid (*b. p.* 193°). It is a stronger base than aniline, and readily combines with acids, forming salts. Being a secondary amine, it reacts with nitrous acid, forming **nitroso-methylaniline.** $C_6H_5(NO)CH_3$, a yellow oily liquid, which gives Liebermann's nitroso reaction (chap. 30, sec. 8, reac. 2, p. 453). When methylaniline hydrochloride is heated, it yields a mixture of *p-* and *o-* toluidines (sec. 2, method 5, p. 600).

19. Dimethylaniline, $C_6H_5N(CH_3)_2$.—This compound is prepared on a large scale by heating aniline hydrochloride with an excess of methyl alcohol in an autoclave (methylation):

$$C_6H_5.NH_2HCl + 2CH_3OH \rightarrow C_6H_5.N(CH_3)_2HCl + 2H_2O$$

The product is treated with milk of lime to set free the base, which is then separated by distillation in steam.

Dimethylaniline is an oily liquid of a peculiar odour. It boils at nearly the same temperature (192°) as methylaniline. It is an even stronger base than methylaniline. It combines with alkyl halides, yielding *quaternary ammonium salts.* The hydrochloride of dimethylaniline, on being heated, yields 2,4-xylidine (sec. 2, method 5, p. 600).

The para-hydrogen atom of dimethylaniline is extraordinarily reactive. For this reason, it shows a number of characteristic reactions which *differentiate* it from aliphatic as well as from purely aromatic tertiary amines:

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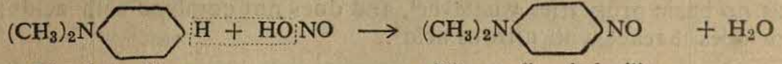
[1] The presence of three electronegative phenyl groups in the molecule entirely destroys the basic nature of ammonia.

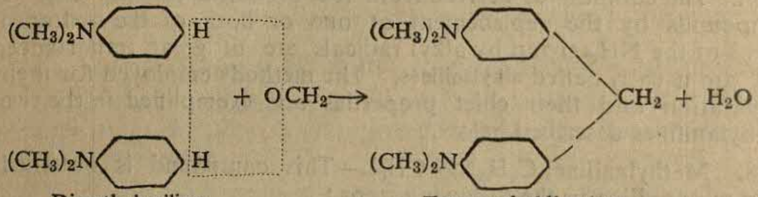
[2] These characters are shared by other purely aromatic tertiary amines. They either fail to react with nitrous acid, or undergo nitration in the nucleus.

(1) It reacts with nitrous acid, yielding intensely green *p*-**nitrosodimethylaniline.**



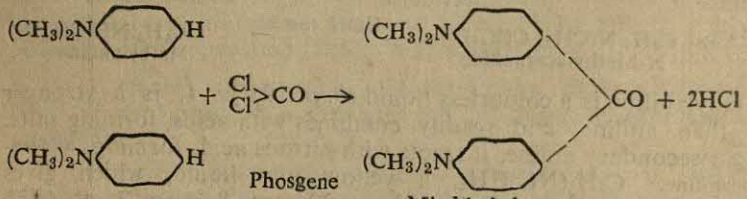
Dimethylaniline *p*-Nitroso-dimethylaniline

(2) It undergoes condensation with formaldehyde to give **tetramethyldiaminodiphenylmethane** :—



Dimethylaniline (2 molecules) Tetramethyldiaminodiphenylmethane

(3) Similarly, it reacts with phosgene, yielding **Michler's ketone :**



Phosgene

Mischler's ketone

Use. Dimethylaniline is extensively used in the manufacture of dyes.

20. *p*-**Nitrosodimethylaniline,** $(CH_3)_2<\overline{\underline{\quad}}>NO$, is prepared, as already stated, by the action of nitrous acid on dimethylaniline. It crystallizes in leaves or plates having fine, intense green colour (*m.p.*, 85°).

Reactions. (1) *p*-Nitrosodimethylaniline combines with hydrochloric acid, yielding a hydrochloride, which crystallizes in yellow needles.

(2) On reduction with zinc-dust, it gives *p*-**aminodimethylaniline,** a compound extensively used in the manufacture of dyestuffs.

(3) When boiled with sodium hydroxide, the amino group of *p*-nitrosodimethylaniline is replaced by hydroxyl, *p*-nitrosophenol and dimethylamine being produced.

$$(CH_3)_2N<\overline{\underline{\quad}}>NO + HOH \rightarrow HO<\overline{\underline{\quad}}>NO + HN(CH_3)_2$$

The reaction is used in the preparation of pure dimethylamine.

IV. ARYL-SUBSTITUTED ALIPHATIC AMINES

As already stated, the members of this group **closely resemble aliphatic amines** in modes of preparation and properties. The best known representative of this class is benzylamine.

21. Benzylamine, $C_6H_5CH_2NH_2$.—Benzylamine may be obtained by methods analogous to those employed for the preparation of aliphatic primary amines ; *e.g.*, (*i*) by the action of ammonia on benzyl chloride,

$$C_6H_5CH_2Cl + NH_3 \rightarrow C_6H_5CH_2NH_2,HCl$$

(*ii*) by the reduction of phenyl cyanide,

$$C_6H_5CN + 4H \rightarrow C_6H_5CH_2NH_2$$

(*iii*) from phenylacetamide, by the bromamide reaction,

$$C_6H_5CH_2CONH_2 \xrightarrow{Br + KOH} C_6H_5CH_2NH_2$$

Properties. Benzylamine is a colourless, pleasant smelling liquid. It readily dissolves in water, yielding a strong alkaline solution.

It forms salts with acids, gives carbylamine reaction, and, when treated with nitrous acid, it gives benzyl alcohol and *not* a diazo-compound.

22. **Dibenzylamine,** $(C_6H_5CH_2)_2NH$, and **tribenzylamine,** $(C_6H_5CH_2)_3N$, are examples of secondary and tertiary amines belonging to this group. They may be obtained by heating benzylamine with benzyl chloride,

$$C_6H_5CH_2NH_2 + C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_2NH.HCl$$

$$C_6H_5CH_2NH_2 + 2C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_3N{\cdot}HCl + HCl$$

They closely resemble aliphatic secondary and tertiary amines in chemical behaviour.

QUESTIONS

1. How do you distinguish the three classes of aromatic amines from one another ? Compare these with those of aliphatic series. (*Karnatak, B.Sc., 1961*)

2. Give an account of the properties and reactions of aniline including the action of the following reagents : (*a*) bromine, (*b*) nitrous acid, (*c*) acetyl chloride, (*d*) formaldehyde, (*e*) alkyl halides. (*Ajmer, B.Sc., 1961*)

3. Describe the laboratory preparation of aniline. Starting from aniline, how would you obtain (*a*) benzene, (*b*) sulphanilic acid, (*c*) phenol, (*d*) iodobenzene? Give equations. (*Gauhati, B.Sc., 1961*)

4. Give different industrial methods to prepare aniline. Starting with aniline how would you prepare any two of the following :

(*i*) Diphenylamine, (*ii*) Sulphanilic acid, (*iii*) Iodobenzene and (*iv*) *p*-nitroaniline. (*Baroda, B.Sc., 1962*)

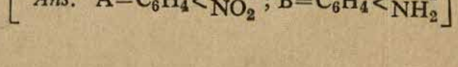
5. How is aniline prepared in the laboratory ? How would you convert aniline into phenol, chlorobenzene, and phenylhydrazine ? Explain the reactions involved. (*Annamalai, B.Sc., 1962*)

6. A colourless crystalline solid was found to contain C=71·1%, H=6·7%, N=10·4%. On boiling the substance with concentrated hydrochloric acid and adding an excess of KOH, an oily liquid was obtained, which gave a violet coloration with a solution of sodium hyprochlorite. What was the original substance ?

[*Ans.* Acetanilide, $C_6H_5NHCOCH_3$]

7. On combustion, 0·357 gm. of an organic compound, *A*, gave 0·561 gm. of CO_2 and 0·077 gm. of water. The compound contains 16·7 per cent of nitrogen. On reduction it gave a derivative, *B*, having the following percentage composition: C=52·2, H=4·35, N=20·3, O=23·15. The compound *B* forms a hydrochloride containing 20·92 per cent of hydrochloric acid. Find the formulae of *A* and *B*.

(*Punjab, B.Sc., Hons. 1926*)



$$\left[\ \textit{Ans.}\ A=C_6H_4{<}\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}\ ;\ B=C_6H_4{<}\begin{smallmatrix}NO_2\\NH_2\end{smallmatrix}\right]$$

8. The following results were obtained by analysing a mono-acid organic base.

0·100 gm. gave 0·2882 gm. of CO_2 and 0·0756 gm. of H_2O.
0·200 gm. gave 21·8 ml. of N_2 at 15° and 760 mm. pressure.
0·400 gm. of the platinichloride left on ignition 0·125 gm. of platinum.

Find the melecular formula of the compound, and suggest a constitutional formula for it. *(Punjab, B.Sc., 1935)*

$$\left[\textit{Ans.}\ \ C_7H_3N\ ;\ C_6H_5CH_2NH_2\ \text{or}\ C_6H_4{<}^{CH_3}_{NH_2} \right]$$

9. Give an account of the properties and reactions of aniline including the action of the following reagents: (*a*) bromine, (*b*) nitrous acid, (*c*) acetyl chloride, (*d*) formaldehyde, (*e*) alkyl halides. *(Rajasthan, B.Sc., 1961)*

10. An organic base (A) A was found to contain C=72·7 per cent, H=9·1 per cent, N=8·5 per cent. It forms a nitrosoamine on treatment with nitrous acid. On exhaustive methylation, it gave a product $C_9H_{10}O$ (B) which was oxidised by permanganate to an acid $C_8H_8O_3$ (C). The latter on heating with hydrochloric acid yielded methyl iodide and an acid $C_7H_6O_3$ (D) which on heating with soda-lime gave phenol. The acid (C) gave two isomeric mono-nitro derivatives. Discuss the constitution of (A). *(Bombay, B.Sc., 1950)*

11. How is aniline prepared in industry ? Compare and contrast the reactions of aniline with those of ethylamine ? *(Lucknow, B.Sc., 1953)*

12. Describe with practical details the preparation of aniline. How does aniline react with nitrous acid at low temperature ? Describe how this reaction is utilised for the synthesis of aromatic compounds. *(Bihar, B.Sc., 1954)*

13. What are the chief methods for the preparation of aromatic amines ? Give their important reactions. *(Jammu & Kashmir, B.Sc., 1954)*

14. In what important aspects does aniline differ from ethylamine ? Starting from aniline, how would you prepare (*a*) benzene, (*b*) phenol, (*c*) bromobenzene, (*d*) phenyl cyanide and (*e*) phenylhydrazine ? *(Banaras, B.Sc., 1955)*

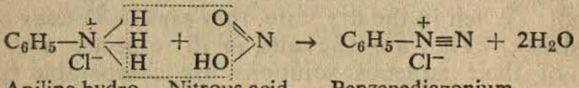
15. Describe the laboratory method for the preparation of aniline. How would you prepare (*a*) benzene, (*b*) phenol, (*c*) sulphanilic acid and (*d*) chlorobenzene ? *(Andhra, B.Sc., 1956)*

CHAPTER FORTY-FOUR

DIAZONIUM SALTS AND RELATED COMPOUNDS

1. DIAZONIUM SALTS

1. Diazotization of Amino Compounds.—The most characteristic property of an aromatic amino-compound having the amino group in direct union with the nucleus, is that when a *well-cooled* aqueous solution of one of its salts is treated with nitrous acid, a **"diazonium salt"** is produced. This process is termed **diazotization** :



$$C_6H_5-\underset{Cl^-}{\overset{+}{N}}\begin{smallmatrix}H\\H\\H\end{smallmatrix} + \begin{smallmatrix}O\\HO\end{smallmatrix}\!>\!N \rightarrow C_6H_5-\underset{Cl^-}{\overset{+}{N}}\equiv N + 2H_2O$$

Aniline hydrochloride Nitrous acid Benzenediazonium chloride

It should be carefully noted that the essential change involved in the reaction is the conversion of the phenylammonium *ion* $C_6H_5NH_3^+$, into the **benzenediazonium ion** :—

$$\left\{C_6H_5NH_3\right\}^+ \xrightarrow{HNO_2} \left\{C_6H_5N\equiv N\right\}^+$$

The above reaction, called **diazo-reaction**, was discovered by Griess in 1858, and is perhaps the most important reaction in the chemistry of aromatic compounds. The diazonium salts are of great importance in organic syntheses and in the manufacture of dyes, since they undergo a number of remarkable reactions.

2. Preparation of Diazonium Salts.—(1) The diazonium salts may be obtained in *crystalline* state by treating a well-cooled solution of a primary amino-compound in absolute alcohol with amyl nitrite[1] and a mineral acid, the reaction being carried out, as far as possible, in the *absence* of water. Thus to prepare **benzenediazonium sulphate** the following procedure is adopted.

Aniline (1 mole) is dissolved in absolute alcohol, and concentrated sulphuric acid (excess) is added to the solution. The mixture is cooled in a freezing mixture, and pure amyl nitrite (1 mole) is gradually run in from a tap-funnel. On allowing the reaction mixture to stand for about 15 minutes, crystals of benzene diazonium sulphate separate out. They may be washed with alcohol and ether, and dried in air at the ordinary temperature.

Crystals of the **benzenediazonium chloride** may be obtained in a similar manner, hydrogen chloride being used instead of sulphuric acid. **Benzenediazonium nitrate**[2] is best obtained by passing nitrogen trioxide (generated by heating nitric acid and arsenious oxide) into a solution of aniline in dilute nitric acid. On adding alcohol and ether, crystals of the nitrate separate out.

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[1] Amyl nitrate is here used instead of sodium nitrite because of its solubility in alcohol.

[2] Benzenediazonium nitrate is violently explosive, and it is *not* advisable to prepare more than half a gram in the dry state.

2a. Preparation of Diazonium Salt Solution.—Since a diazonium salt in the dry state is very explosive, and since most of the reactions, that it undergoes, readily take place in aqueous solution, it is almost invariably prepared in aqueous solution. The amino-compound is dissolved in an excess of a mixture of equal volumes of concentrated hydrochloric acid and water, and the mixture is well-cooled by means of ice. A well-cooled aqueous solution of sodium nitrite is gradually run in from a dropping funnel, the end of which dips under the solution to be diazotized. Throughout the addition, the mixture is well stirred and the temperature not allowed to rise. The addition of sodium nitrite is continued, until a drop of the reaction mixture gives an *immediate* blue colour when placed upon starch-potassium iodide paper, showing the presence of free nitrous acid.

3. Physical Properties of Diazonium Salts.—Diazonium salts are colourless crystalline substances, very readily soluble in water, less so in alcohol. When in the dry state, they **explode violently** on being heated or struck. They are true salts, in all respects, and the conductivities of their aqueous solutions are comparable to those of the ammonium salts.

4. Reactions of Diazonium Salts.—The reactions of the diazonium salts may be divided into twn groups, (A) and (B), as given below.

(*A*) Replacement of the Diazonium Group.—$N^+{\equiv}N$. By treating aqueous solutions of diazonium salts with different reagents, the diazo-group is readily replaced by other substituents, **nitrogen being set free in the gaseous state.** The following are the more important substitution reactions :

(1) **Replacement by hydrogen.** When the solution of a diazonium salt is warmed with an alkaline solution of stannous chloride, the diazo group gets replaced by a hydrogen atom, and an aromatic hydrocarbon is produced :

$$\underset{\substack{\text{Benzene-diazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + 2H \rightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + HCl$$

When a *dry* diazonium salt is heated with alcohol, there occurs, in addition to the formation of an ether (reaction 2), a replacement of the N_2X group by hydrogen with the production of an aromatic hydrocarbon, the alcohol being oxidized to acetaldehyde :

$$C_6H_5N_2Cl + CH_3CH_2OH \rightarrow C_6H_6 + N_2 + HCl + CH_3CHO$$

(2) **Replacement by hydroxyl, alkoxyl, or acyloxyl group.** When the aqueous solution of a diazonium salt is warmed, hydrolysis of the compound occurs with the production of a phenol :

$$C_6H_5N_2Cl + HOH \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

When a dry diazonium salt is heated with an alcohol or a fatty acid, an ether or an ester is produced :

$$C_6H_5N_2Cl + HOC_2H_5 \rightarrow \underset{\text{Phenyl ethyl ether}}{C_6H_5OC_2H_5} + N_2 + HCl$$

$$C_6H_5N_2Cl + HO.CO.CH_3 \rightarrow \underset{\text{Phenyl acetate}}{CH_3COOC_6H_5} + N_2 + HCl$$

(3) **Replacement by iodine.** When a solution of a diazonium salt is warmed with potassium iodide, the corresponding iodo derivative is produced :

$$\underset{}{C_6H_5N_2Cl} + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + N_2 + KCl$$

This reaction is often employed as a preparative method for iodo compounds.

(4) **Replacement by chlorine, bromine or the cyanogen group.** When a solution of a diazonium salt is warmed with a solution of cuprous chloride in hydrochloric acid, the diazo group is replaced by a chlorine atom, and a chloro derivative of an aromatic hydrocarbon results :

$$C_6H_5N_2Cl + (CuCl) \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2 + (CuCl)$$

Similarly, when we use a solution of cuprous bromide in hydrobromic acid or a solution of potassium cuprocyanide, we get respectively the bromo and the cyano derivative :

$$C_6H_5N_2Cl + CuBr \longrightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2 + CuCl$$

$$C_6H_5N_2Cl + CuCN \longrightarrow \underset{\text{Phenyl cyanide}}{C_6H_5CN} + N_2 + CuCl$$

A reaction like the above, in which a cuprous salt plays the part of a catalyser, is known as **Sandmeyer's reaction.** A modification of it, known as **Gattermann's reaction,** is based on the use of finely divided copper in place of the cuprous salt.

The conversion of diazonium salts into cyano compounds is of great importance, as the cyano compounds, on hydrolysis, yield the aromatic acids.

$$\underset{\text{Benzonitrile}}{C_6H_5CN} + 2H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3$$

(5) **Replacement by nitro group.** Diazonium salts in aqueous solution are decomposed by nitrous acid in the presence of cuprous oxide to give nitro compounds :—

$$C_6H_5N_2Cl + HNO_2 \xrightarrow{Cu_2O} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + N_2 + HCl$$

Hodgson and Marsden's method (1944), which gives particularly good results, consists in converting the diazonium salts into diazonium cobaltinitrites, *e.g.*, $(C_6H_5N_2)_3[Co(NO_2)_6]$, and decomposing the latter with cuprous oxide and cupric sulphate.

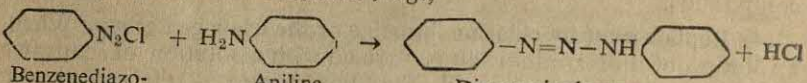
(*B*) **Reactions with Retention of Nitrogen.** In the second group of reactions of diazonium salts, the nitrogen atoms remain intact. There are three chief reactions belonging to this category.

(1) **Reduction to hydrazines** When a diazonium salt is submitted to reduction with stannous chloride in hydrochloric acid solution, a *monosubstituted aromatic hydrazine* is produced :—

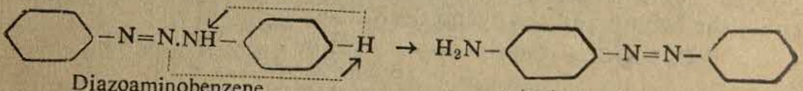
$$\underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + 4H \rightarrow \underset{\substack{\text{Phenylhydrazine}\\\text{hydrochloride}}}{C_6H_5NHNH_2,HCl}$$

(2) **Coupling reactions.** Diazonium salts undergo an important and characteristic reaction, known as "**coupling**", with aromatic compounds in which the benzene ring has been "activated" by the presence of an amino group, $-NH_2$, a substituted amino-group $-NHR$ or $-NR_2$, or an $-OH$ group.

(*i*) Primary and secondary aromatic amines react with diazonium salts to give **diazoamino compounds** ; *e.g.*,

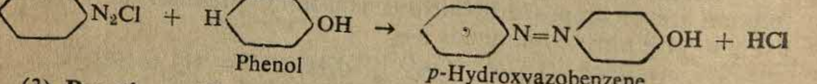


The most interesting property of diazoamino compounds is their isomerization into **aminoazo compounds**, the arylazo group migrating to the *para* position in the ring. This occurs on heating with a small quantity of a mineral acid or aniline hydrochloride which act as catalysts:

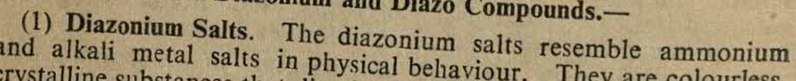


***p*-Aminoazobenzene** is the parent substance of a large number of azo dyes. It is employed as the first component, and, after being diazotized, is coupled with phenolic compounds of the naphthalene group.

(*ii*) Tertiary aromatic amines couple with diazonium salts to give directly aminoazo compounds :—



(*iii*) Similarly, phenols couple with diazonium salts in presence of alkalis to form hydroxyazo compounds:—



(3) **Reaction with alkalis to form diazotates.** This involves a tautomeric change, and is discussed in the next section.

5. Structure of Diazonium and Diazo Compounds.—

(1) **Diazonium Salts.** The diazonium salts resemble ammonium and alkali metal salts in physical behaviour. They are colourless, crystalline substances that dissolve in water to form solutions that possess high electrical conductivity. The aqueous solutions of aryl-diazonium chlorides, sulphates and nitrates are neutral to litmus, while those of the carbonates are alkaline (compare sodium carbonate). Like ammonium salts, they form platichlorides, *e.g.*, $(C_6H_5N_2)_2PtCl_6$. For these reasons, the diazonium salts are assigned the formula $[C_6H_5-\overset{+}{N}\equiv N]X^-$, in which the **diazonium ion**, like the ammonium ion,

$(NH_4)^+$, is monovalent positive. Of the two nitrogen atoms, one is tricovalent and the other tetracovalent.

The formation of diazonium salts (sec. 1) and their substitution reactions are in full agreement with the diazonium structure.

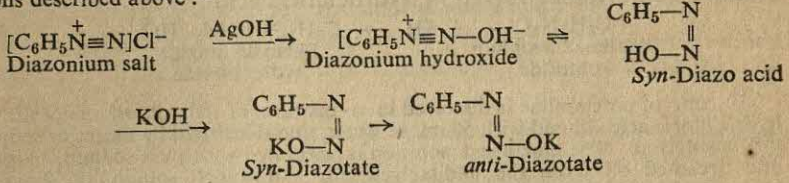
(2) **Diazo Compounds.** When silver hydroxide (one equivalent) is added to a solution of a diazonium chloride or barium hydroxide to that of a diazonium sulphate, a strongly alkaline solution is produced, which is assumed to contain a **diazonium hydroxide**, $(C_6H_5-N\equiv N,OH$. The base cannot, however, be isolated on account of its being highly unstable.

When sodium hydroxide is added to a diazonium hydroxide solution, there occurs a fall in the electrical conductivity of the solution, which is supposed to be due to the formation of a salt, called a **sodium diazotate**. Since a strong base, like benzenediazonium hydroxide, could not itself react with a strong alkali like sodium hydroxide, it is assumed that the diazonium hydroxide undergoes a **tautomeric change** to give a **diazo hydroxide**, $C_6H_5—N=N—OH$. The latter substance behaves like a weak *acid* and forms a **sodium diazotate**.

When an *excess* of alkali is added to the solution containing a sodium diazotate, the latter passes into the isomeric **sodium isodiazotate**, which can be isolated in the solid form. While the normal diazotates react with phenols to give azo-dyes, isodiazotates do not react.

It is thus clear that diazonium salts are stable in acid solutions, normal diazotates in approximately neutral solutions and isodiazotates in alkaline solutions.

According to Hantzsch, the normal diazotates and iso-diazotates are *cis*- and *trans*-isomers respectively. The following scheme represents the transformations described above :—



$$\underset{\text{Diazonium salt}}{[C_6H_5\overset{+}{N}\equiv N]Cl^-} \xrightarrow{AgOH} \underset{\text{Diazonium hydroxide}}{[C_6H_5\overset{+}{N}\equiv N—OH^-} \rightleftharpoons \underset{\textit{Syn}\text{-Diazo acid}}{\begin{array}{c}C_6H_5—N\\ \|\\ HO—N\end{array}}$$

$$\xrightarrow{KOH} \underset{\textit{Syn}\text{-Diazotate}}{\begin{array}{c}C_6H_5—N\\ \|\\ KO—N\end{array}} \rightarrow \underset{\textit{anti}\text{-Diazotate}}{\begin{array}{c}C_6H_5—N\\ \|\\ N—OK\end{array}}$$

6. Uses of Diazonium Salts.—

(1) Diazonium salts are of great importance in synthetic organic chemistry, and are used in the preparation of numerous derivatives of aromatic hydrocarbons (refer to Reactions). Since the diazonium salts are obtained from the nitro-compounds, *via* the amino compounds, it is obvious that nitration of aromatic substances is a reaction of first rate importance, for, with the help of the diazo-reactions, the nitro-group may be replaced by almost any desired group.

(2) The great importance of diazonium salts in industry is shown by an almost unlimited number of azo-dyes placed on the market.

II. DIAZOAMINO AND AMINOAZO COMPOUNDS

7. **Diazoaminobenzene,** $C_6H_5N_2.NHC_6H_5$.—This is a typical example of the diazoamino compounds. It is conveniently prepared by treating aniline in alcoholic or acetic acid solution with nitrous acid. The diazonium compound, produced in the first instance, reacts with the excess of aniline present to give diazoaminobenzene. The latter is separated from the reaction mixture by adding sodium acetate crystals. The product is washed with water and dried on a porous plate.

Diazoaminobenzene crystallizes in brilliant golden yellow needles melting at 98°. It is sparingly soluble in water, but dissolves readily in alcohol, ether and light petroleum. It is only feebly basic, and does not form stable salts with acids. As already stated, it may be converted into aminoazobenzene by isomerization.

8. ***p*-Aminoazobenzene,** $<\!\overline{\quad}\!>N{=}N<\!\overline{\quad}\!>NH_2$.—This important compound is prepared on a large scale from aniline *via* diazoaminobenzene, as described above. It may also be prepared by nitrating azobenzene, and reducing the resulting *p*-nitroazobenzene with ammonium sulphide.

Aminoazobenzene crystallizes from alcohol in brilliant orange-red plates, melting at 123°. Being basic in nature, it forms salts with acids. These are highly coloured.

Aminoazobenzene is used as a first component in preparing other azo dyes; after being diazotized, it is coupled with phenolic compounds of the naphthalene group. Aminoazobenzene hydrochloride, $<\!\overline{\quad}\!>N{=}N<\!\overline{\quad}\!>NH_2,HCl$, which forms beautiful grey-blue needles, is sometimes used as a silk dye under the name of **aniline yellow.**

III. HYDRAZINES

9. Aryl hydrazines are classified in the same way as the aliphatic hydrazines. Of the *monosubstituted* hydrazines, the most important is phenylhydrazine described below. A typical example of a *symmetrical disubstituted* aromatic hydrazine is hydrazobenzene, $C_6H_5NH.NHC_6H_5$.

10. Phenylhydrazine, $C_6H_5.NH.NH_2$.

Preparation. (1) This compound is usually prepared in the laboratory by the reduction of benzenediazonium chloride by means of stannous chloride dissolved in hydrochloric acid :

$$\underset{\substack{\text{Benzenediazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} + 4H \rightarrow \underset{\substack{\text{Phenylhydrazine}\\ \text{hydrochloride}}}{C_6H_5.NH.NH_2,\ HCl}$$

10 gm. of pure aniline is dissolved in a mixture of 50 ml. of concentrated hydrochloric acid diluted with 50 ml. of water, and diazotized by means of sodium nitrite solution. The diazotized solution is saturated with pure sodium chloride, and decanted off from the undissolved salt. An ice-cold solution of 50 gm. of stannous chloride ($SnCl_2.2H_2O$) in 25 ml. of concentrated hydrochloric acid is gradually added. The precipitate of phenylhydrazine stannichloride, which rapidly forms, is allowed to stand in contact with the liquid for a few hours. It is then filtered by means of Buchner funnel, washed with a little concentrated hydrochloric acid, and decomposed with sodium hydroxide solution. Phenylhydrazine, which separates as an oily liquid, is extracted with ether, and the ethereal solution dehydrated over anhydrous potassium carbonate. The ether is distilled off, and the phenylhydrazine is purified by distillation under reduced pressure.

(2) Phenylhydrazine is prepared on a large scale by converting the diazonium salt into sodium diazobenzenesulphonate by means of sodium sulphite, reducing the product with zinc-dust and acetic acid, and eliminating the sulphonic group by boiling with hydrochloric acid :

I. $$\underset{\substack{\text{Benzenediazonium}\\ \text{chloride}}}{C_6H_5N{\equiv}NCl} + Na_2SO_3 \rightarrow \underset{\substack{\text{Sodium diazobenzene-}\\ \text{sulphonate}}}{C_6H_5N{=}NSO_3Na} + NaCl$$

II. $$C_6H_5N{=}NSO_3Na + 2H \rightarrow \underset{\substack{\text{Sodium phenylhydrazine-}\\ \text{sulphonate}}}{C_6H_5.NH.NH.SO_3Na}$$

III. $$C_6H_5.NH.NH.SO_3Na + HOH \rightarrow \underset{\text{Phenylhydrazine}}{C_6H_5NH.NH_2} + NaHSO_4$$

In actual practice, the intermediate products are not separated. The solutions of the diazonium salt and sodium sulphite are mixed together, acetic acid and zinc-dust are added, and when the reaction is over, the excess of zinc is filtered off. The filtrate is boiled with fuming hydrochloric acid, when the hydrochloride, $C_6H_5NH.NH_2HCl$, being almost insoluble in hydrochloric acid, separates out.

Physical Properties. Phenylhydrazine is a colourless, oily liquid which turns brown in air, and boils with slight decomposition at 241°. On cooling, it solidifies to give large, colourless crystals (*m.p* , 23°). Phenylhydrazine is only slightly soluble in water.

Reactions. (1) Phenylhydrazine is a basic substance, and combines with acids to form well-defined, crystalline salts, *e.g.*, $C_6H_5NH.NH_2HCl$ or $C_6H_5NH.NH_3Cl$.

(2) It is an active reducing agent, and precipitates cuprous oxide from Fehling's solution *in the cold* :

$$C_6H_5.NH.NH_2 + 2CuO \rightarrow C_6H_6 + N_2 + Cu_2O + H_2O$$

The reaction is *quantitative*, and is used for the **estimation of phenylhydrazine**, the volume of nitrogen set free being measured. Another importance of the reaction lies in its utilization for converting nitrobenzene, aniline, or a diazonium salt into *benzene*.

(3) When treated with energetic reducing agents (zinc-dust and hydrochloric acid), phenylhydrazine yields aniline and ammonia :

$$C_6H_5NH.NH_2 + 2H \rightarrow C_6H_5NH_2 + NH_3$$

The reaction establishes the **constitution of phenylhydrazine.**

(4) Phenylhydrazine is an important reagent for aldehydes and ketones. It has also been much used by Fischer in the study of sugars.

(5) Phenylhydrazine undergoes condensation with acetoacetic ester, and the product, when heated with methyl iodide, yields **antipyrine**, a substance used in medicine as a febrifuge.

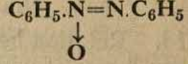
Uses. (1) Large quantities of phenylhydrazine are employed in the manufacture of *antipyrine*.

(2) As already stated, it is much used in the laboratory as a reagent for aldehydes, ketones and sugars.

IV. AZOXY, AZO AND HYDRAZO COMPOUNDS

These compounds are formed by the reduction of nitro compounds in *alkaline* solution. We shall restrict ourselves to the compounds derived from benzene.

11. Azoxybenzene.—This compound is generally prepared by boiling, under a reflux condenser nitrobenzene with a solution of sodium methoxide in methyl alcohol.



$$C_6H_5.\underset{\overset{\downarrow}{O}}{N}=N.C_6H_5$$

Properties. (1) Azoxybenzene crystallizes in pale-yellow needles (*m.p.* 35°). It is insoluble in water, but readily soluble in organic liquids.

(2) When distilled with iron filings, it yields azobenzene.

(3) When warmed with concentrated sulphuric acid, it isomerizes into *p-hydroxyazobenzene*, $C_6H_5.N{=}N.C_6H_4OH$.

12. Azobenzene, $C_6H_5.N{=}N.C_6H_5$.—As already mentioned, azobenzene is prepared by distilling azoxybenzene with iron filings. It forms brilliant, orange-red crystals (*m.p.* 68° ; *b.p.* 295°), insoluble in water.

When reduced with an alkaline reducing agent, such as ammonium sulphide or zinc-dust and alcoholic potash, azobenzene is converted into *hydrazobenzene*,

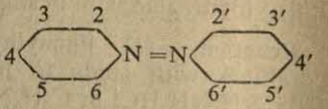
$$C_6H_5.N{=}N.C_6H_5 + 2H \rightarrow C_6H_5.NH.NH.C_6H_5\ ;$$

while with acid-reducing agents, such as zinc-dust and acetic acid, the molecule breaks up, yielding two molecules of *aniline* :

$$C_6H_5N{=}NC_6H_5 + 4H \rightarrow 2C_6H_5NH_2$$

On oxidation with hydrogen peroxide in glacial acetic acid, azobenzene is converted into azoxybenzene.

The importance of azobenzene lies in its being the substance from which a large number of dyes (known as *azo dyes*) are derived. In naming these compounds, the positions of substituents are indicated as shown in the margin.



13. **Hydrazobenzene,** $C_6H_5NH.NH.C_6H_5$.—Hydrazobenzene which may be regarded as *symmetrical diphenylhydrazine*, is prepared, as stated above, by the reduction of azobenzene with zinc-dust and potash. It may also be prepared directly from nitrobenzene by reduction with zinc-dust and sodium ethoxide.

Properties. (1) Hydrazobenzene crystallizes in colourless plates (*m. p.* 130°).

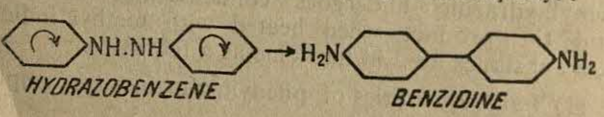
(2) It is readily oxidized to azobenzene under the action of mild oxidizing agents (*e.g.*, HgO or air).

(3) When subjected to energetic reduction it gives aniline.

(4) On being heated, it undergoes decomposition in such a way that one molecule is *oxidized* to azobenzene at the expense of a second molecule that is *reduced* to aniline (2 molecules) :—

$$2C_6H_5.NH.NH.C_6H_5 \rightarrow C_6H_5.N{=}N.C_6H_5 + 2C_6H_5NH_2$$

(6) When treated with concentrated mineral acids, hydrazobenzene undergoes a remarkable intramolecular change, whereby the benzene nuclei are, so to say, turned end for end. The product is **benzidine**, or *p-diaminodiphenyl* :



Because of the ready conversion of hydrazobenzene into benzidine, it is the latter compound that is produced when azobenzene is reduced in acid solution.

The intramolecular transformation just described is termed **"benzidine transformation,"** and is characteristic of all hydrazo compounds in which the two *para*-positions are free. If both the *para*-positions be already occupied, the change does *not* take place. This proves that in benzidine the two amino groups occupy the para-position.

V. AZO DYES

14. **Relation between Colour and Constitution (Witt's Theory).**—When a ray of white light is passed through a prism, it is spread out into a spectrum, which consists of a smooth transition of colour from red, through orange, yellow, green, blue and indigo, to violet. The red end of the spectrum consists of light of the longest wave-length (about 8,000 Angstrom units) that the eye is capable of detecting, while the violet end represents the other limit of visibility (wave-lengths of approximately 4,000 Angstrom units). White light is evidently a mixture of the above seven colours in such proportions

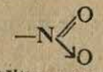
that the visual effect is that of ordinary white light. If this white light is passed through or reflected from the surface of a substance having an absorption band in the visible region of the spectrum, one or more of the spectrum colours will be eliminated, and, in that case, the emergent or reflected light will appear coloured.

The visual effect of white light can also be obtained by mixing together two *complementary colours*, as shown in the table given in the margin. If, therefore, any one of the colours is removed from the spectrum, the remaining light will give the visual effect of the complementary colour. Thus, indigo blue has a strong absorption band in the *yellow* region of the visible spectrum ; it is therefore that it possesses an indigo colour when seen in white light.

COMPLEMENTARY COLOURS

Violet	Green-yellow
Indigo	Yellow
Blue	Orange
Blue-green	Red
Green	Purple

Chromophores. All substances possess absorption bands, the number of which varies considerably. The bands may or may not fall in the *visible* region of the spectrum. It is only in the former case that the substance possesses colour. Let us consider benzene, which from the point of view of the theory of colour is of considerable interest. The substance, because it transmits all the visible light through it without absorption, is colourless. In the ultra-violet region of the spectrum of benzene, however, there does exist a complex absorption band. It has been shown by Otto Witt that if various unsaturated groups are introduced into the benzene molecule, new visible absorption bands come into being, and some of these may fall into the region of the spectrum, thus giving rise to a coloured substance. Such groups that displace or bring into being absorption bands in the visible region of the spectrum have been termed by Witt "**Chromophores**", *i.e. colour-bearers.* The most important chromophores, all of which represent unsaturated structures, are—



$-\mathrm{N}\begin{matrix}{}^{\nearrow}\mathrm{O}\\ {}_{\searrow}\mathrm{O}\end{matrix}$

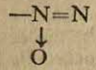
Nitro group

$-\mathrm{N}=\mathrm{O}$

Nitroso group

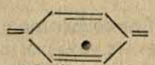
$-\mathrm{N}=\mathrm{N}-$

Azo group

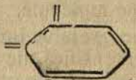


$\begin{array}{l}-\mathrm{N}=\mathrm{N}\\ \;\;\downarrow\\ \;\;\mathrm{O}\end{array}$

Azoxy group



p-Quinonoid structure



o-Quinonoid structure

Hence, while benzene is colourless, nitrobenzene, nitrosobenzene, azobenzene, azoxybenzene, *p*-benzoquinone and *o*-benzoquinone are all coloured. As has already been stated, the chromophores are unsaturated groups. If the group is reduced to a saturated structure the colour vanishes. Thus, aniline, hydrazobenzene, quinol and catechol are all colourless. It must not, however, be assumed that the relationship is so simple and that the colour produced by a given chromophore or chromophores can be predicted with any certainty. This is by no means the case, and the effect is never additive. A substance having a chromophoric group in its molecule is termed a "**chromogen**".

The *ortho*- and *para*-quinonoid structures are powerful chromophores, and triphenylmethane dyes (as also the pink colour of phenolphthalein in alkaline solution) owe their colour property to the presence of the quinonoid grouping. This association of colour with the quinonoid structure is often referred to as the **quinonoid theory of colour**.

Auxochromes. All coloured substances do not behave as dyes. Thus, if a piece of cloth be dipped in a solution of azobenzene, the fabric takes up but little of the colour, and even that little is easily washed out again. Witt established the fact that a coloured substance could only act as a dye if it had the property of forming a salt-like compound with the material which it was dyeing. A **salt forming group** that must enter the molecule of a chromogen before it could act as a dye is termed by Witt an "**auxochrome**". The common auxochromes are the OH, NH_2, NHR, and NR_2 groups. It is interesting to note that the carboxyl and the sulphonic acid groups do *not* possess the characters of an auxochrome. From this it is clear that the auxochrome are as specific by nature as the chromogens. Perhaps the best example illustrating Witt's theory is afforded by aminoazobenzene. $C_6H_5{=}NC_6H_4NH_2$. Here the chromophore group is the azo group $-N{=}N-$; the chromogen is azobenzene, $C_6H_5N{=}NC_6H_5$, which is not itself a dye, but it becomes so by the introduction of the NH_2 auxochrome, *i.e.*, the NH_2 radical.

The term "**deepening of colour**" signifies, in this connection. the progressive shifting of absorption bands from the violet region through the red end of the spectrum, on to the green-yellow region, thus giving rise to the complementary colours in the reverse order :—

Green-yellow → Yellow → Orange → Red → Purple →
Violet → Indigo → Blue → Green-blue → Green

A radical that brings about a deepening of colour is termed a "**bathocrome**" and the one that produces the opposite effect (*i.e.* a *lightening* of colour) is called a "**hypsochrome**". It has been found that auxochrome groups are, in general. excellent bathochromes. The progressive introduction of auxochrome groups. whereby the colour usually deepens, affords, therefore, a convenient means of producing dyes having different colours or shades of colour. Thus alizarin has two auxochrome OH groups and is red ; on introducing 2 more OH groups into the molecule we get a dye having a deep red colour; while the introduction of three more OH groups results in the formation of a deep-violet dye. The acetyl group is an example of a hypsochrome. Dyestuffs containing OH or NH_2 groups become much lighter in colour on acetylation.

The **chief points of Witt's Theory** may be summarized as follows :—

1. The character of a dye is derived from some characteristic grouping, called a "**chromophore**", present in the molecule.

2. The fundamental substance containing the chromophore (*e.g.*, azobenzene) is termed the "**chromogen**".

3. The chromogen, though a coloured substance, is not a dyestuff, but it becomes a dyestuff when a salt-forming group, termed an "**auxochrome**", is introduced into the molecule.

4. The progressive introduction of auxochrome groups into the molecule of a dye usually intensifies the colour, or, as we say, possesses a "**bathochromic effect**". Certain radicals, on the other hand, have an opposite effect ; they bring about a lightening of colour, and are termed **hypsochromes**.

15. Classification of Dye-stuffs.—Dyes are divided into a number of groups, based upon their constitution and methods of manufacture. The chief of these groups are—

(1) Azo dyes ;
(2) Di- and tri-phenylmethane dyes
(3) Indigo and indigoid dyes ;
(4) Alizarin and related dyes ;
(5) Sulphur dyes.

16. Azo Dyes.—Azo dyes contain the chromophore $-N{=}N-$. They are derived from the chromogen azobenzene, $C_6H_5N{=}NC_6H_5$, which, as already stated, possesses an orange-red colour. It is, however, not itself a dye, since it is not possible to fix it on cloth.

By introducing in the molecule of azobenzene (or any other chromogen containing one or more azo groups), auxochrome groups $-NH_2$, NHR, $-NR_2$, $-OH$, etc., numerous derivatives are obtained which possess valuable dyeing properties. These are known as azo dyestuffs or azo dyes.

Preparation. Azo dyes are prepared by the reaction known as **coupling.** The substances that are coupled to form an azo dye are termed the **components**. The first component, that is, the one that is diazotized, may be any compound containing a primary amino group, NH_2, *directly* attached to an aromatic nucleus. The second component, that is, the one with which the diazonium ion couples, may be selected from a great variety of phenolic and arylamino compounds including primary, secondary and tertiary amines, $ArNH_2$, ArNHR, $ArNR_2$. Hence, numerous azo dyes may be made by the use of a very large number of the two kinds of components that are available. In fact, thousands of azo dyes have been prepared in this way in the laboratory and hundreds of these are being manufactured on the commercial scale.

Manufacture. A diagrammatic sketch of the plant employed in the manufacture of azo dyes is shown in Fig. 1 The solution of the amine (1 mol) in hydrochloric acid (2 mols) is placed in a large wooden vat of about 2,000 gallon capacity and provided with a mechanically driven wooden stirrer. The solution is cooled to 0°—5° by the addition of crushed ice, and the nitrite solution is gradually run in, the process being carefully watched by means of starch-iodide and congo red test papers. When the diazotization is complete, the diazotized solution

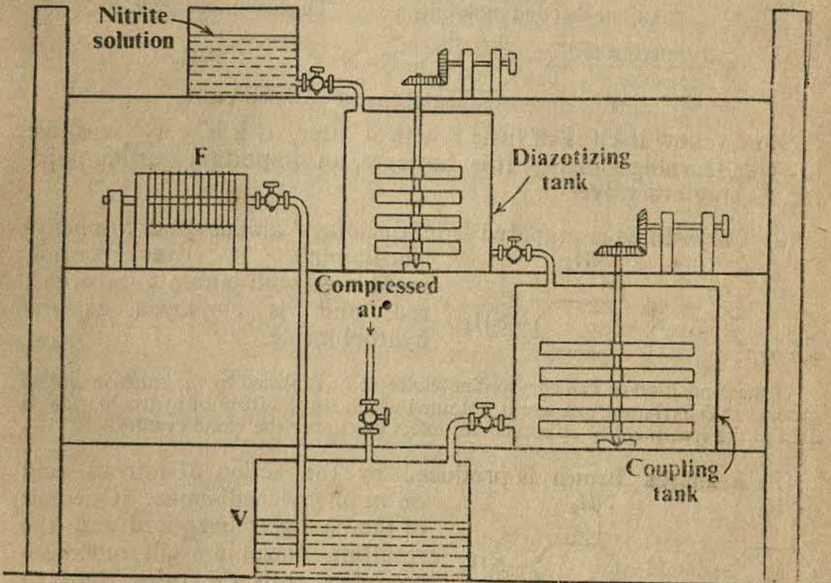


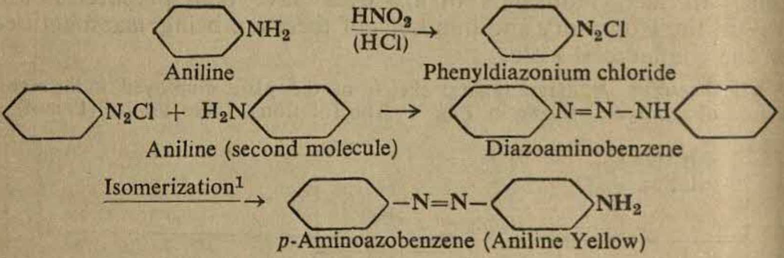
Fig. 1. Plant for the manufacture of Azo-Dyestuffs.

is run by gravity into the *coupling tank* (capacity 5,000 gallons), which contains an alkaline solution of a phenol or its sulphonic acid (or an aqueous solution of an aromatic amine hydrochloride). Interaction between the two solutions occurs with the production of an azo dyestuff, which remains largely in solution. Hence common salt is added to completely throw the dyestuff out of solution. The liquid, along with the dyestuff, is now transferred to the vessel *V*, whence it is blown by compressed air to the filter press, *F*. The dyestuff is then taken out of the press, dried and powdered.

17. Example of Azo Dyes.—A few simple examples of azo dyes are given below :—

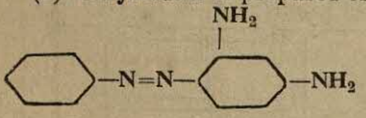
(*a*) **Basic Azo dyes.** The examples of this class are :—

(1) **Aniline Yellow** (*p*-Aminoazobenzene) is the simplest of the azo dyes, and was the first to be prepared (Griess, 1859). The diazotizing and the coupling component in this case is one and the same substance, *viz.* aniline :—



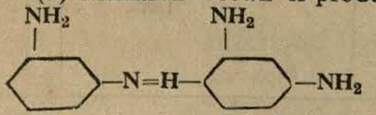
Aniline yellow itself is of little practical value, as it is very sensitive to acids (turning violet). It is, however, an important starting point for making other dyes.

(2) **Chrysoidine** is prepared from diazotized aniline and *m*-phenylenediamine. It dyes cotton mordanted with tannin a brownish red, and is employed as the hydrochloride.



If the *p*-position in the chrysoidine molecule be replaced by the sulphonoamido group, $-SO_2NH_2$. an azo dye is obtained which (in the form of hydrochloride) is used in the treatment of streptococcal infections under the name **Prontosil.**

(3) **Bismarck Brown** is produced by the action of nitrous acid on *m*-phenylenediamine. One-half of the base gets diazotized and the resulting diazonium salt undergoes coupling with the other half to produce the dye. The hydrochloride, which is a dark brown powder, is used in dyeing leather (directly) and cotton (mordanted with tannin). Bismarck brown is also used for the synthesis of poly-azo dyes.



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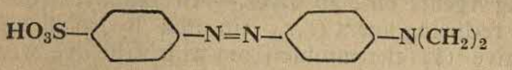
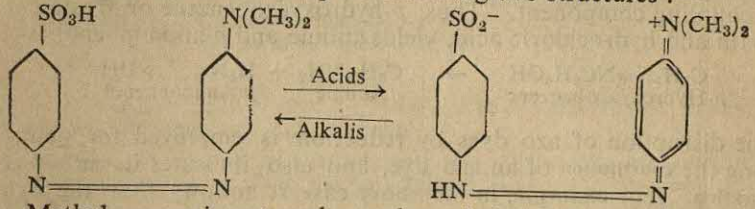
[1] See page 618.

(*b*) **Acid Azo Dyes** :—

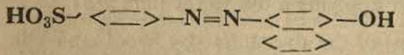
(1) **Methyl Orange, Helianthine,** or **Orange III,** obtained by coupling diazotized sulphanilic acid with dimethylaniline hydrochloride, is a tautomeric substance having the following two structures :—



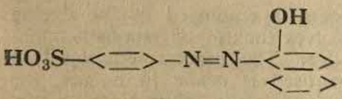


Methyl orange is not used as a dye. It is highly sensitive to acids, and, for that reason, is employed as an **indicator in acidimetry.**

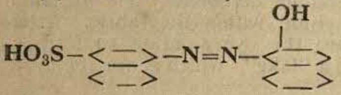
(2) α-**Naphthol Orange,** or **Orange I,** is obtained by coupling diazotized sulphanilic acid with α-naphthol. It dyes wool and silk directly.



(3) β-**Naphthol Orange,** or **Orange II,** is prepared by coupling diazotized sulphanilic acid with β-naphthol. It is similar to, and more commonly used orange dye than, α-naphthol orange.

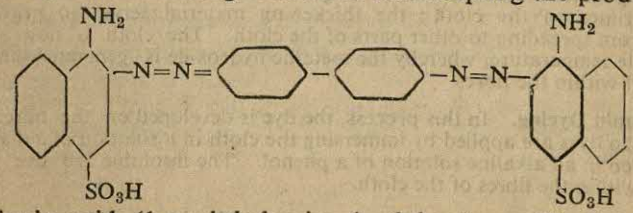


(4) **Fast Red A,** obtained by coupling diazotized naphthionic acid with β-naphthol. It is a very cheap red acidic dye, and is fast to washing.



18. Bis-azo Dyes.—Many valuable dyestuffs have been prepared by diazotizing *p*-diamines and coupling the resulting **bisdiazonium salts,** with amines and phenols. The most important group of these bis-azo dyestuffs includes those derived from *benzidine*.

Congo Red is one of the best known dyes of this group. It is obtained by bisdiazotizing benzidine and coupling the product with naphthionic acid (1-naphthylamine-4-sulphonic acid) in alkaline solution. The actual dyestuff is the sodium salt of the acid thus formed. It is a scarlet red powder, which, on the addition of acids, turns blue.



Congo red possesses the valuable property of dyeing unmordanted cotton.

19. Action of Reducing Agents on Azo Dyes.—An azo dye when treated with an energetic reducing agent (*e.g.*, tin and hydrochloric acid) breaks down to give (1) the amine from which the dye was originally obtained by diazotization, and (2) the amino derivative of the coupling component. Thus, *p*-hydroxyazobenzene on treatment with tin and hydrochloric acid, yields aniline and *p*-aminophenol :—

$$\underset{p\text{-Hydroxyazobenzene}}{C_6H_5N{=}NC_6H_4OH} \rightarrow \underset{\text{Aniline}}{C_6H_5.NH_2} + \underset{p\text{-Aminophenol}}{H_2N\langle\underline{\quad}\rangle OH}$$

The disruption of azo dyes by reduction is employed for determining the **constitution** of an azo dye, and also indicates its **method of preparation.** For example, in the above case it follows that the dye (*p*-hydroxyazobenzene) was obtained by diazotizing aniline and coupling it with phenol, and further that, in the formation of the dye, the coupling occurred in *para*-position to the phenolic group.

20. Dyeing.—The various processes for applying a dye to the fibre are :

(1) **Direct or Substantive Dyeing.**—Most of the dye-stuffs dye wool and silk directly. They are usually acidic or basic in nature, and form insoluble compounds with the proteins of animal fibres (silk and wool).

(2) **Indirect or Adjective Dyeing.** This process is employed in the dyeing of vegetable fabrics (cotton and linen), and involves the use of **mordants**—substances which combine chemically with the dye. The process employed in adjective dyeing is as follows . If the dye to be used is *acidic* in nature, the cloth is first dipped in a solution of a salt of a weak base, *e.g.*, aluminium acetate, ferric alum, etc. It is then exposed to the action of steam, or is treated with a solution of a weak alkali, such as ammonia or sodium carbonate. The metallic hydroxide is thus deposited in a fine state of division within the fabric. After being thus *mordanted*, the cloth is dipped into the dye solution to form a coloured, insoluble adsorption compound, called a "**lake**", which is not removed by washing.

In dyeing with *basic* dyes, an acid mordant, such as *tannin*, is used. In most cases, the process is completed by treatment with a solution of tartar emetic. Pink salt, $(NH_4)_2SnCl_6$, is also used as a mordant with basic dyes. The cloth, after being dipped in a solution of this salt, is exposed to the action of steam, whereby stannic acid, $SnO_2.xH_2O$, is set free, and combines with the basic dye.

In **calico-printing** a solution of a dye is mixed with a suitable mordant and a thickening material, such as starch or gum. With this mixture, the required design is printed on the cloth ; the thickening material serves to prevent the mordant from spreading to other parts of the cloth. The cloth is now steamed at a suitable temperature, whereby the metallic hydroxide is generated and fixes the dyestuff within the fibres.

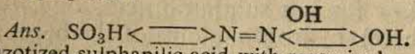
(3) **Ingrain Dyeing.** In this process, the dye is developed on the fibre. Thus insoluble azo dyes are applied by immersing the cloth in a solution of a diazonium salt and then in an alkaline solution of a phenol. The insoluble azo dye is thus produced within the fibres of the cloth.

(4) **Vat Dyeing.** Vat dyes include those coloured substances that are insoluble in water, but on reduction readily form derivatives that are soluble in dilute alkali. These reduction products, by their subsequent re-oxidation on the fabric, are converted into the original insoluble dyes. The process of vat-dyeing is explained in detail in the case of indigo.

QUESTIONS

1. What are the diazonium salts? How are they prepared? Describe their important reactions, and write a short note on the structure of diazonium compounds. (*Punjab, B.Sc., 1947*)

2. An orange-yellow dye when submitted to the action of tin and hydrochloric acid gave a mixture of sulphanilic acid and dihydroxyaniline. The latter component, when treated with sodium nitrite and hydrochloric acid, yielded hydroxyquinol (1,2,4-triyhdroxybenzene) on heating the reaction mixture. What conclusion do you draw as to the constitution of the dye and the method by which is was prepared?



Ans. $SO_3H<\underline{\quad\quad}>N=N<\overset{OH}{\underline{\quad\quad}}>OH$. The dye was obtained by coupling diazotized sulphanilic acid with resorcinol.

3. Give an account of diazo compounds with special reference to their structure and reactions. Point out the similarity between the reactions of Alkyl and Diazonium chlorides. (*Lahore, B.Sc., 1958*)

4. What is diazo reaction? Discuss its application in organic synthesis. Employing the diazo reaction, give the synthesis of any two azo dyes. (*Poona, B.Sc., 1956*)

5. Discuss the application of the diazo reaction in organic synthesis. How has this reaction been used in industry? (*Bombay, B. Sc., 1951*)

6. What do you understand by diazotisation? Show how with the help of this reaction various substituents can be introduced into the benzene nucleus. (*Bombay, B.Sc., 1958*)

7. How is benzenediazonium chloride prepared in solution? What is its action with $SnCl_2$ & HCl, $SnCl_2$ & NaOH, β-napthol dissolved in NaOH, KI, cuprous bromide and HBr, alkaline solution of phenol. (*Agra, B.Sc., 1958*)

8. Describe the preparation of benzenediazonium chloride and show how it can be used for the synthesis of benzene, phenol, benzonitrile, and phenylhydrazine. Write equations. (*Calcutta, B.Sc., 1960*)

9. Describe fully the structure of aromatic diazo compounds. (*Utkal, B.Sc., 1960*)

10. Describe the preparation of benzenediazonium chloride in the laboratory. With suitable examples, explain the synthetical applications of benzenediazonium chloride. (*Mysore, B.Sc, 1960*)

11. What is the diazo reaction? How is an aromatic amine diazotised? Describe the various reactions of diazo compounds. (*Jubalpur, B.Sc., 1960*)

12. Describe the preparation of phenylhydrazine and explain its use in chemistry of aldehydes and ketones. (*Karnatak, B.Sc., 1960*)

13. Give the synthetic uses of Diazonium Salts. (*Lucknow, B Sc., 1962*)

14. Discuss the constitution of Diazonium Salts. (*Lucknow, B.Sc. 1959*)

15. Discuss the structure of phenyl-diazonium chloride.

Show how it is converted to—

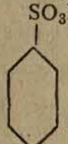
(*i*) Benzene, (*ii*) phenol, (*iii*) phenyl ethyl ether, (*iv*) iodobenzene, (*v*) phenyl cyanide, (*vi*) phenyl isocyanate. (*Bombay, B.Sc., Chemistry, Subs., 1963*)

STATE INSTITUTE OF EDUCATION

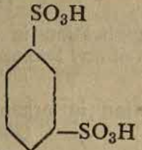
CHAPTER FORTY-FIVE

AROMATIC SULPHONIC ACIDS

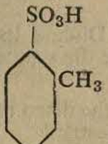
1. General.—When benzene, its homologues and their derivatives are treated with sulphuric acid or fuming sulphuric acid, one, two or three (never more than three) hydrogen atoms of the benzene nucleus get replaced by the **sulphonic group**, $-SO_2OH$ or $-SO_3H$. The products are called **sulphonic acids** and the process **sulphonation**. The following are some examples of sulphonic acids :



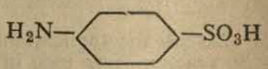
Benzenesulphonic acid



Benzene-*m*-disulphonic acid



Toluene-*o*-sulphonic acid



Aniline-*p*-sulphonic acid

2. Sulphonation of Aromatic Compounds.—Sulphonation of aromatic compounds may be carried out with concentrated sulphuric acid, fuming sulphuric acid (containing varying proportions of SO_3), chlorosulphonic acid and sulphuryl chloride, or with a mixture of concentrated sulphuric acid and actic anhydride.

(*i*) **Monosulphonation of Benzene.** When benzene is sulphonated with concentrated sulphuric acid in the cold, a large excess of the acid is required, as the water produced in the reaction,

$$C_6H_6 + H_2SO_4 \rightleftharpoons C_6H_5SO_3H + H_2O,$$

dilutes the acid to below its effective strength (65% H_2SO_4). The difficulty is overcome by **passing benzene vapour through sulphuric acid heated to 170°—180°.** The water produced in the reaction is thus evaporated off as soon as formed, and the whole of the sulphuric acid is converted into benzenesulphonic acid.

(*ii*) **Monosulphonation of an Alkylbenzene.** When a homologue of benzene is submitted to sulphonation, the *para*-compound is produced as the major product together with some *ortho*-compound. The addition of mercuric sulphate considerably increases the yield of the ortho-compound.

(*iii*) **Disulphonation.** On sulphonating benzene with fuming sulphuric acid at 200°—250°, *meta*-disulphonic acid is obtained as the chief product. On prolonged heating with sulphuric acid, the meta-compound is partially converted into the *para*-compound. In fact, a state of equilibrium between the two isomers is established.

(*iv*) **Trisulphonation.** Prolonged sulphonation, especially in the presence of silver sulphate as the catalyst, yields trisulphonic acids of benzene and its homologues. It has not been found possible, so far, to introduce more than three —SO_3H groups in the benzene nucleus by direct sulphonation.

Separation of the Product.—

(1) From the strongly acidic reaction mixture, sulphonic acids may separate out as crystals on cooling.

(2) If, on cooling, the sulphonic acid does not crystallize out, it may be separated from the mixture containing excess of sulphuric acid by the addition of common salt, until no more of the salt will dissolve. Under these conditions, the sulphonic acid is precipitated as its sodium salt. This is separated, dissolved in water, the solution treated with an equivalent quantity of a mineral acid, and the free sulphonic acid extracted with ether.

(3) Another method of separating sulphonic acids is based on the solubility of their barium salts in water, the process being similar to the separation of ethyl hydrogen sulphate from sulphuric acid.

3. **Technical Importance.**—The process of sulphonation is of great technical importance, especially in the manufacture of dyes. This is based on the ready solubility of sulphonic acids, and more particularly of their sodium salts, in water. Many compounds of beautiful colour, that cannot be used as dyes, because of their insolubility in water, are rendered available for dyeing purposes after sulphonation.

4. **Manufacture.**—The technical preparation of sulphonic acids is carried out in a large, enamelled or lead-lined pan (Fig. 1). This is usually provided with an outer jacket through which steam or cold water can be circulated to control the temperature. If the compound to be sulphonated is volatile, the pan is also fitted with a reflux condenser (compare technical preparation of aniline). At the end of the operation the charge is blown by compressed air into water contained in large vats, and the sulphonic acid is recovered either as such or as the sodium salt.

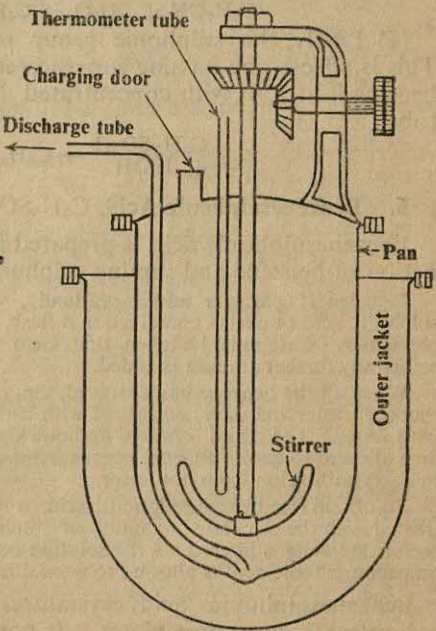


Fig. 1. Sulphonation Pan.

5. Properties and Chemical Behaviour.—

(1) Sulphonic acids are colourless, crystalline substances, very readily soluble in water, and are usually hygroscopic and deliquescent in moist air.

(2) They are strong acids, and their salts including the barium salts, are soluble in water.

(3) When a sulphonic acid is treated with phosphorus pentachloride, the hydroxyl part of the sulphonic group is replaced by chlorine with the production of *sulphonyl chloride* :

$$\underset{\text{Benzenesulphonic acid}}{C_6H_5SO_2OH} + PCl_5 \longrightarrow \underset{\text{Benzenesulphonyl chloride}}{C_6H_5SO_2Cl} + POCl_3 + HCl$$

(4) When fused with an alkali hydroxide, sulphonic acids lose a molecule of sulphur dioxide, and give *phenols* (compare carboxylic acids, which lose a molecule of carbon dioxide similar treatment) :—

$$C_6H_5SO_3K + KOH \longrightarrow C_6H_5OH + K_2SO_3$$

The reaction is of great technical importance.

(5) When their potassium salts are distilled with potassium cyanide, the corresponding nitriles are produced :

$$C_6H_5SO_3K + KCN \rightarrow C_6H_5CN + K_2SO_3$$

The reaction may be utilized for synthesizing aromatic acids :

$$C_6H_5CN + 2H_2O \rightarrow C_6H_5COOH + NH_3$$

(6) Lastly, the sulphonic group may be replaced by *hydrogen.* This is effected by passing superheated steam into the acid, or by heating it at 150° with concentrated hydrochloric acid in a sealed tube :

$$\begin{array}{l} C_6H_5\vdots SO_3H \\ +\ H\,OH \end{array} \rightarrow C_6H_6 + H_2SO_4$$

6. Benzenesulphonic Acid, $C_6H_5SO_2OH$ or $C_6H_5SO_3H$.—

Benzenesulphonic acid is prepared in the laboratory by the interaction of benzene and fuming sulphuric acid.

Benzene (1 part) is added gradually, with continued shaking, to fuming sulphuric acid (4 parts) contained in a flask, the latter being fitted with a reflux condenser. Care must be taken that each quantity of benzene gets dissolved before any further amount is added.

When all the benzene has dissolved, the reaction mixture is poured into an excess of water and then neutralized with barium carbonate made into a thin paste with water. The liquid is heated and quickly filtered through a fluted filter, and then allowed to cool. Barium benzenesulphonate that crystallizes out is purified by recrystallization from hot water.

To obtain free benzenesulphonic acid, a weighed amount of the crystals is treated with the calculated quantity of dilute sulphuric acid. The precipitated barium sulphate is filtered off, the solution evaporated to a small bulk and the benzenesulphonic acid is allowed to crystallize, preferably in a desiccator.

Benzenesulphonic acid crystallizes from water with $1\frac{1}{2}H_2O$ in colourless, hygroscopic plates. It possesses all the chemical characters of an aromatic sulphonic acid.

Benzenesulphonic acid is employed in the manufacture of metanilic acid.

7. **Benzene-*m*-disulphonic acid** (*m.p.*, 63°), mixed with a little **benzene-*p*- disulphonic acid** (*m.p.*, 32°), is formed when benzene is heated with fuming sulphuric acid.

When toluene is submitted to sulphonation, *o*- and *p*-**toluene sulphonic acids** are obtained.

8. Sulphonyl Chlorides and Sulphonamides.—The *chlorides* of aromatic sulphonic acids are obtained by the action of phosphorus pentachloride on the acids. They may also be prepared directly by the action of chlorosulphonic acid on aromatic hydrocarbons :

$$C_6H_6 + HO\,SO_2.Cl \rightarrow C_6H_5SO_2Cl + H_2O$$

Aromatic sulphonyl chlorides possess a disagreeable odour, and are very stable towards cold water, being decomposed extremely slowly. When treated with excess of concentrated ammonia, they are converted into *sulphonamide* :

$$C_6H_5SO_2Cl + 2NH_3 \rightarrow C_6H_5SO_2NH_2 + NH_4Cl$$

The sulphonamides are well-crystallized substances, and determination of their melting points are frequently employed for the identification of sulphonic acids. On account of the strongly negative character of the group $C_6H_5SO_2$—, the hydrogen atoms of the NH_2 group are replaced by metals. The sulphonamides are therefore soluble in alkalis.

Benzenesulphonyl chloride, $C_6H_5SO_2Cl$, melts at 14·5° to give a liquid that boils at 251°. It is employed in **Hinsberg's method for the separation of amines** (p. 450).

QUESTIONS

1. Describe the preparation and reactions of benzenesulphonic acid. Explain how benzene, phenol and phenyl cyanide may be obtained from it. (*Rajasthan B Sc., 1961*)

2. How is benzenesulphonyl chloride prepared and purified ? Mention its chief use. (*Rajasthan, B.Sc., 1960*)

3. Describe the methods of preparation, properties and technical importance of aromatic sulphonic acids. (*Gujarat, B.Sc., 1958*)

4. Write an account of the sulphonating agents used in aromatic chemistry.

How will you convert —SO_3OH group into (*i*) —OH, (*ii*) —CN, (*iii*) —SO_2NH_2 and (*iv*) H ? (*Baroda, B.Sc., 1962*)

5. Give equations illustrating the chemical reactions of benzenesulphonic acid. (*Madras, B.Sc , 1954*)

6. Describe the preparation of aromatic sulphonic acids and give examples of their synthetic uses especially in preparing hydroxy, cyano and chloro derivatives of benzene.

Indicate clearly the constitutional relationship between saccharin and sulphonic acids. (*Punjab, B Sc., 1955*)

7. Give the synthesis of Saccharin. (*Bombay, B.Sc., Subs., 1956*)

8. Give the preparation from benzene of benzene-sulphonic acid. How is it converted into phenol, benzoic acid and benzenesulphonamide ? (*Mysore, B.Sc., 1957*)

9. How can benzene sulphonyl chloride be prepared ? Describe its importance in the separation of a mixture containing primary, secondary and tertiary amines. (*Allahabad, B.Sc., 1958*)

10. Describe the preparation of benzene sulphonic acid. How will you prepare (*i*) benzonitrile, (*ii*) phenol, (*iii*) benzene, and (*iv*) benzenesulphonamide from it ? (*Poona, B.Sc., 1960*)

11. Discuss the structure of the sulphonic acid group in benzenesulphonic acid. (*Patna, B.Sc., 1961*)

CHAPTER FORTY-SIX

AROMATIC ARSENIC COMPOUNDS

1. Chemotherapy. The term "*chemotherapy*" is applied to the branch of medicine that aims at the selective destruction of disease-producing germs *within* the animal body by chemical agents. The definition excludes disinfectants (which act externally), and a host of drugs having physiological effects on various organs of the human body. At the beginning of the 20th century, only three specific remedies were known : (1) Mercury for syphilis, (2) Cinchona bark for malaria, and (3) ipecacuanha for amoebic dysentry.

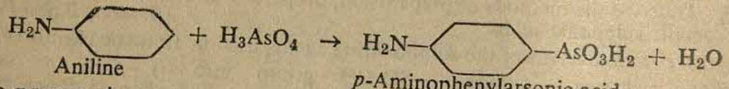
The pioneer in the field of modern chemotherapy was a German physician, **Paul Ehrlich** (1854—1915), who devoted most of his time to the idea that a molecule can be constructed which can act as s specific agent against a parasite without injuring the host. As the result of his researches quite a number of specific drugs (more particularly, aromatic arsenic compounds) were discovered that have proved extremely useful.

The chief classes of chemotherapic agents now in use are: (*i*) Organic arsenicals, (*ii*) Amoebicidal drugs, (*iii*) Antimalarials, (*iv*) Sulpha drugs, and (*v*) Antibacterials of microbial origin.

2. Aromatic Arsonic Acids.—The starting point in the synthesis of arsenicals is the aromatic arsonic acids. They contain the monovalent **arsonic acid group**, —AsO_3H_2 directly united to an aromatic nucleus.

Preparation. There are two methods in use for the preparation of arsonic acids :—

(1) By fusion of an aromatic amino compound, or a phenol, with arsenic acid, *e.g.*,

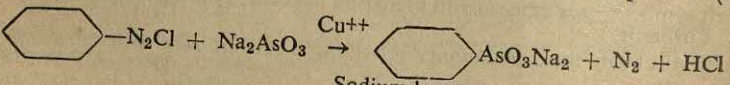


Aniline

p-Aminophenylarsonic acid

The process is analogous to the sulphonation of aromatic compounds.

(2) By the action of arsenious acid, or an arsenite, on a diazonium salt in the presence of a trace of cupric sulphate (**Bart Reaction**) :—

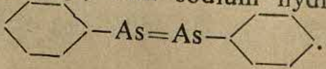


Sodium benzenearsonate

Properties. Aromatic arsonic acids are colourless, crystalline substances. They possess the usual aromatic characters.

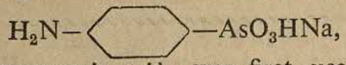
When submitted to **reduction**, they give the following products :—

(*i*) Controlled reduction (*e.g.*, with sulphurous acid) results in the production of **arylarsenic oxides**, (*e g.*, benzenearsenic oxide. C_6H_5—AsO).

(*ii*) More vigorous reduction (*e.g.*, with sodium hydrosulphite) produces **arseno compounds**, *e.g.*, .

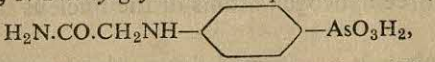
(*iii*) Prolonged energetic reduction with nascent hydrogen leads to the formation of arylarsines (*e.g.* $C_6H_5AsH_2$).

3. Some Important Arsenicals.—Of a large number of aromatic arsenic compounds, the following have found use in medicine.

Atoxyl, 

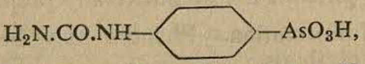
the monosodium salt of *p*-aminobenzenearsonic acid, was first used by Robert Koch for the treatment of African sleeping sickness. Contrary to what is indicated by the name "*atoxyl*", this compound is too toxic for practical use, even when modified in the form of derivatives.

Tryparsamide, *N-Phenylglycineamide-p-arsonic acid,*



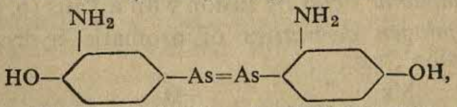
is perhaps the most effective remedy for sleeping sickness. It has also proved valuable in the treatment of neurosyphilis.

Carbarsone, *p-Ureidobenzenearsonic acid,*



is closely related to tryparsamide, and is very effective in amoebic dysentry.

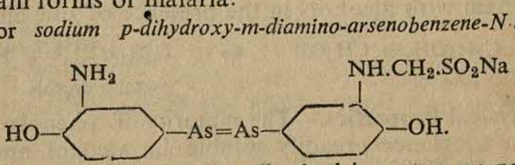
Salvarsan, *3,3'-Diamino 4,4'-dihydroxy arsenobenzene,*



was discovered by Ehrlich in 1910 and called by him **"606"**[1]. The drug was patented in Germany under the name "Salvarsan". During World War I, the patent was taken over by United States of America and the name changed to **arsphenamine.**

Arsphenamine is used for the treatment of syphilis, and is also effective in certain forms of malaria.

Neosalvarsan, or *sodium p-dihydroxy-m-diamino-arsenobenzene-N methylene-sulphinate,*



is preferred to salvarsan, because, when dissolved in water, or normal salt solution, it is suitable for injection without further treatment.

Metallic derivatives of salvarsan and neosalvarsan, such as *copper salvarsan, silver salvarsan, silver neosalvarsan,* have also been shown to possess great therapeutic value.

QUESTIONS

1. How are aromatic arsonic acids prepared? Give their chief properties.
2. Write notes on (*a*) atoxyl, (*b*) carbarson, (*c*) Salvarsan, and (*d*) neosalvarsan.
3. Write an account of the aromatic arsenic compounds.
4. Write a note on Chemotherapy.

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[1] This, it is said, denotes the number in the series of compounds prepared by Ehrlich in slowly and steadily approaching his objective.

CHAPTER FORTY-SEVEN

PHENOLS

1. Phenols are derived from aromatic hydrocarbons by the replacement of *nuclear* hydrogen by one or more hydroxyl groups. They are termed *monohydric*, *dihydric* or *trihydric* phenols according as one, two or three hydrogen atoms of the nucleus have been thus replaced.

Monohydric phenols are formed during the destructive distillation of wood and coal. Hence they are present in wood-tar and coal-tar. It is from the latter source that ordinary phenol (carbolic acid) and other monohydric phenols are commercially prepared.

2. **Methods of Formation.**—Phenols may be prepared by the following general methods :

(1) From *amino compounds* by diazotization followed by warming the aqueous solution (p. 616).

(2) From *sulphonic acids* by fusion with alkalis (p. 632).

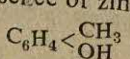
(3) From *halogen derivatives* of aromatic hydrocarbons *via* the Grignard reaction ; *e.g.*,

$$\underset{\text{Bromobenzene}}{C_6H_5Br} \xrightarrow{+Mg} C_6H_5MgBr \xrightarrow{+O} C_6H_5OMgBr \xrightarrow{HOH} \underset{\text{Phenol}}{C_6H_5OH}$$

(4) From *phenolic acids* by heating with soda-lime ; *e.g.*,

$$\underset{\text{Salicylic acid}}{C_6H_4(OH)COOH} + CaO \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + CaCO_3$$

(5) From *lower homologues* by alkylation. This is effected by heating them with alcohols in the presence of zinc chloride ; *e.g.*,



$$\underset{\text{Phenol}}{C_6H_5OH} + CH_3OH \rightarrow \underset{o\text{-and }p\text{-cresols}}{C_6H_4{<}^{CH_3}_{OH}} + H_2O$$

3. **Physical Properties.**—The majority of phenols are colourless, crystalline substances, readily soluble in alcohol and ether. As a rule, the solubility in water increases with the number of hydroxyl groups in the molecule, while the volatility diminishes.

4. **Reactions.**—Reactions of phenols may be discussed under three heads :

(*A*) **Reactions involving Hydroxyl Groups.** They are—

(1) Phenols, like other hydroxy compounds, react with phosphorus pentachloride :—

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

(2) They react with acid anhydrides, yielding *esters*. Thus, when ordinary phenol is heated with acetic anhydride, it gives **phenyl acetate** (*b.p.* 195°), which is hydrolysed even by boiling water.

$$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}{>}O + C_6H_5OH \rightarrow CH_3COOC_6H_5 + CH_3COOH$$

(3) Phenols, like aliphatic alcohols, may be converted into *ethers* by heating their alkali salts with alkyl halides or with bromo derivatives of aromatic hydrocarbons, finely-divided copper being used as a catalyst in the latter case :

$$\underset{\text{Sodium phenate}}{C_6H_5.ONa} + \underset{\text{Methpl iodide}}{CH_3I} \rightarrow \underset{\text{Phenyl methyl ether}}{C_6H_5.O.CH_3} + NaI$$

$$C_6H_5ONa + C_6H_5Br \rightarrow \underset{\text{Diphenyl ether}}{C_6H_5.O.C_6H_5} + NaBr$$

When the vapour of a phenol is passed over thoria heated at 400° to 450°, a simple di-aryl ether is produced :

$$2C_6H_5OH \rightarrow \underset{\text{Diphenyl ether}}{C_6H_5.O.C_6H_5} + H_2O$$

Similarly, when the mixed vapours of a phenol and an alcohol are passed over heated thoria, a mixed ether is produced :

$$C_6H_5OH + C_2H_5OH \rightarrow \underset{\text{Phenyl ethyl ether}}{C_6H_5.O.C_2H_5} + H_2O$$

(4) Owing to the combination of the hydroxyl group with the electronegative benzene ring, phenols possess acidic properties, and dissolve in aqueous alkalis, yielding salts such as **sodium phonolate**, C_6H_6ONa. They are, however, weakly acidic, and their salts with alkalis are decomposed by carbon dioxide (contrast salts of carboxylic acids). The dissolution of phenols in alkalis and their reprecipitation by carbon dioxide is frequently made use of in the separation of phenols from natural or more strongly acidic substances.

The acidic nature of phenols is influenced by the presence of other substituents in the ring. Thus, it is enhanced by the introduction of nitro groups.

(5) A characteristic reaction of phenols is that in aqueous or alcoholic solution they give a violet, green or yellow coloration with **ferric chloride.** Thus, ordinary phenol gives a violet, and carvacrol a green colour.

(6) When a phenol is heated with zinc-dust, it yields the parent hydrocarbon :

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

(7) When a phenol is heated with the double compound of ammonia and zinc chloride ($ZnCl_2NH_3$) at 300°, the hydroxyl group is replaced by an NH_2 group :

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

(*B*) **Reactions involving Substitution in Benzene Ring.** The hydrogen atoms of the benzene ring in a phenol are more readily substituted than those of an aromatic hydrocarbon. Thus, ordinary phenol readily yields *s*-tribromophenol. $C_6H_2(OH)\ Br_3$, with bromine water, and *s*-trinitrophenol (picric acid), $C_6H_2(OH)(NO_2)_3$, with nitric acid. Phenols may be alkylated by heating them with an aliphatic alcohol in the presence of zinc chloride.

(*C*) **Condensation Reactions.** (1) Phenols in alkaline solution undergo coupling with diazonium salts, yielding **azo-dyes.**

(2) Another important reaction of phenols is their condensation with phthalic anhydride. The products obtained, called **phthaleins**, will be described in a later chapter.

Tests of Phenols.—

(1) Reaction with ferric chloride (see page 637, reaction 5).

(2) Most phenols when warmed with concentrated sulphuric acid and a little sodium nitrite, give a dark-coloured product, which, when added to water, produces a red colour. This, on addition of an alkali, changes to intense blue or green (**Liebermann's nitroso reaction**).

Expt. 1. Dissolve a little phenol in warm, concentrated sulphuric acid, and add a piece of sodium nitrite. A dark coloured product is obtained. Pour this into a beaker of cold water ; a reddish liquid is formed. Now alkalify the liquid, with sodium hydroxide. A bluish green solution results.

5. Distinguishing Characters of Phenols and Aliphatic Alcohols.— Phenols differ from aliphatic alcohols in the following important respects :—

(1) Acidic character ;

(2) Reaction with ferric chloride ;

(3) Liebermann's nitroso-reaction ;

(4) Coupling reactions ;

(5) Fluorescein reaction (see sec. 21, expt. 4).

All of these (excepting No. 5) have been described in the preceding section.

I. MONOHYDRIC PHENOLS

6. Phenol, Carbolic Acid, *Hydroxybenzene*, C_6H_5OH.

Occurrence. Phenol occurs in minute quantities in the urine of man and that of the ox. It is the chief constituent of the "middle-oil" fraction of coal-tar distillation.

Manufacture.—

(1) **From "middle oil".** For many years phenol was obtained exclusively from the "middle oil" fraction of the coal-tar distillation. The various steps in the process are :—

(*i*) After crystallizing out and removing naphthalene, the residual oil is agitated with sodium hydroxide solution at about 60°, when the phenols present dissolve as sodium salts.

(*ii*) The liquid is then subjected to steam distillation to remove hydrocarbon impurities.

(*iii*) The residual solution is treated with sulphuric acid or carbon dioxide to set free the phenols.

(*iv*) The liberated phenols are now submitted to fractional distillation. The first fraction, collected at 180° to 183°, consists of crystallizable phenol.

(2) **From Benzene through Sulphonation.** To meet the enormously increased demand during World War I (for the production of the explosive Trinitrophenol), phenol was prepared from benzene through sulphonation followed by hydrolysis. The method has since been improved, and consists of the following steps :—

(*i*) Benzene is heated, under pressure, with concentrated sulphuric acid at 170° to 180°, when benzenesulphonic acid is produced :

$$C_6H_6 + H_2SO_4 \rightleftharpoons C_6H_5SO_3H + H_2O$$

(*ii*) The reaction product is neutralized with sodium carbonate solution, when the sodium salt of the sulphonic acid is formed.

(*iii*) The concentrated solution of sodium benzenesulphonate is added to molten NaOH, when sodium salt of phenol is produced :

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

(*iv*) The sodium salt of phenol is treated with hydrochloric acid to set free the phenol :

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$$

(3) **From Benzene through Chlorobenzene.** A new process for the production of phenol was developed in 1928 by Dow Chemical Company.

A mixture of chlorobenzene and dilute sodium hydroxide solution is heated at 300°C and 200 atmosphere pressure in the presence of a catalyst (small quantities of copper and sodium oleate), when the following reaction occurs :—

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O$$

The reaction is *exothermic*, and the heat of reaction is sufficient to maintain the temperature at the required level.

The reaction product is treated with hydrochloric acid to set free the phenol,

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl.$$

Properties. When pure, phenol is a white, crystalline solid (*m.p.* 43°), which goes pink on exposure to air and light. It is deliquescent, and is liquefied on the addition of even a very small proportion of water. Phenol possesses a very characteristic odour, is highly poisonous, and has a strongly caustic action on the skin.

Reactions. The reactions of phenols in general have already been described. The phenol gives a violet coloration with ferric chloride.

When treated with bromine water, it yields a white precipitate of 2, 4, 6-**tribromophenol** ; the reaction is utilized for the separation and quantitative estimation of phenol. The nitration of phenol, resulting in the formation of *s*-trinitrophenol (**picric acid**), is of commercial importance. The interaction between the sodium salt of phenol and carbon dioxide under pressure is utilized in the manufacture of **salicylic acid.** Another reaction of great commercial importance is the condensation of phenol with formaldehyde in the presence of catalysts (see below). When treated with nitrous acid, it yields *p*-**nitrosophenol,** $NO.C_6H_4.OH$.

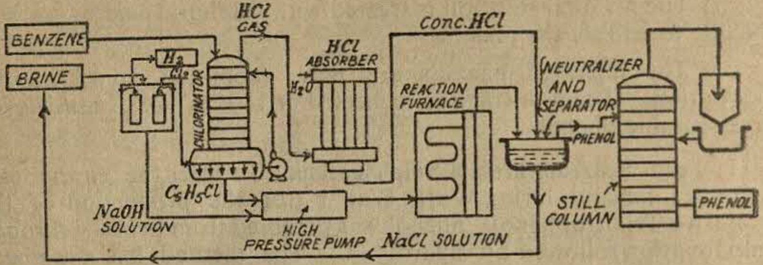


Fig. 1. Manufacture of Phenol from Benzene through chlorobenzene. The starting materials are brine and benzene. The former, by electrolysis, provides chlorine that is used for the chlorination of benzene. The NaOH solution from the electrolytic cell and the chlorobenzene from the chlorinator are together pumped into the reaction furnace. The reaction product containing sodium phenolate is acidified with HCl, derived from the chlorinator, to set free the phenol, which is separated from water by distillation in a vertical still.

Expt. *Tests of Phenol* :—

(1) *Ferric Chloride Test.* To a solution of phenol in water, add a drop of ferric chloride ; violet coloration.

(2) *Phenolphthalein Formation.* Take a crystal of phenol, a little phthalic anhydride, and 1 ml. of conc. H_2SO_4 in a test tube. Heat just above a *small* flame for 2 or 3 minutes. Pour into a beaker half full of water and add NaOH in excess ; intense pink colour of phenolphthalein.

(3) To 1 ml. of phenol solution, add **bromine water,** drop by drop. White ppt. with disappearance of bromine colour.

(4) *Liebermann's Nitroso Reaction.* Dissolve a little of the substance in concentrated H_2SO_4. Add a small piece of sodium nitrite, and pour the product into a beaker of cold water. A reddish colour is produced. Add NaOH in excess. The colour changes to green, blue or violet.

Uses. (1) Phenol is a valuable antiseptic, and is used as a lotion in the dressing of wounds and as a constituent of "carbolic soap". It is also employed for cauterizing the wounds caused by the bite of mad dogs. Other uses of phenol are—

(2) In the manufacture of dyes.

(3) In making picric acid.

(4) In the manufacture of certain medicinal chemicals, such as salicylic acid, salol, aspirin, and phenacetin.

(5) A very important use of phenol is in the manufacture of *bakelite* (sec. 7).

7. Phenol-Formaldehyde Resins—"Bakelite".—Bakelite belongs to a class of "**thermosetting resins**" which are characterized by the fact that they are fusible at some stage of their manufacture, but, under the influence of heat and pressure, ultimately get hard and infusible. The change from the fluid to the solid state is *irreversible*. This class of resins are to be distinguished from **thermoplastic resins** (represented by sealing wax) in which the change from the fluid to the solid state is reversible.

Bakelite is obtained by the action of heat on a mixture of phenol and formaldehyde in the presence of ammonia (catalyst). The process was worked out and patented by Baekeland in 1909. The initial product, called *Bakelite A*, is a thick liquid which, on continued heating, changes to a relatively insoluble but fusible solid, called *Bakelite B*. The latter, when subjected to the action of heat and pressure, yields the final product, *Bakelite C*, which is an insoluble and infusible resin.

Bakelite is used in the manufacture of fountain pens, phonograph records, pipestems, ornamental articles and as an insulator in electrical equipment.

8. Durite, an important modification of Bakelite, is obtained by using furfural in place of formaldehyde. Like bakelite, it is used as a molding resin. Curing is rapid at 180°—190°, and moldings can be made very accurately.

Cresol and other phenols are also employed in making bakelite materials.

9. Halogen Derivatives of Phenol.—Phenol can be halogenated, nitrated and sulphonated more readily than benzene. Direct chlorination or bromination of phenol yields, in the first instance, a mixture of *o*- and *p*- **chlorophenols**, $C_6H_4(OH)Cl$, or **bromophenols**, C_6H_4-(OH)Br. In aqueous solution, the halogenation results in the production of a polyhalogen derivative. Thus, as already mentioned, addition of bromine water to an aqueous solution of phenol causes the precipitation of 2,4,6-**tribromophenol**. When a chloro- or a bromophenol is fused with an alkali, the halogen atom gets replaced by the hydroxyl group, but the position taken up by the hydroxyl group may be different[1] from that occupied by the halogen atom. The introduction of halogen considerably strengthens the acidic character of phenol. Thus, trichlorophenol can bring about the decomposition of carbonates.

10. Nitrophenols.—Nitration of phenol with dilute nitric acid yields *o*- and *p*- **nitrophenols** (*m. p.* 45° and 114°). The two isomerides can be readily separated by steam distillation, only the ortho-compound being volatile. *m*-**Nitrophenol** (*m. p.* 16°) may be prepared from *m*-nitraniline by the diazo-reaction.

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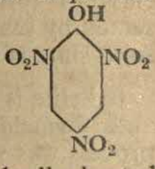
[1] Thus, each of the three bromo-phenols yields resorcinol (1.3-dihydroxybenzene).

Nitrophenols are more acidic than phenols. Their alkali salts cannot be decomposed by carbonic acid. In fact, these salts can be prepared by dissolving alkali carbonates in aqueous solutions of the phenols.

11. Picric acid, 2,4,6-*trinitrophenol,* is the most important nitrophenol derivative. It is manufactured by dissolving phenol (1 part) in concentrated sulphuric acid (4 parts, of sp. gr. 1·84), and adding the solution, in small quantities at a time, to cold concentrated nitric acid (7·5 parts, of sp. gr. 1·38). The temperature is kept at about 10°C throughout the addition. At the end of the operation, the reaction mixture is gradually heated to 80°, till no more brown fumes are evolved. On allowing to cool, picric acid crystallizes out. It is separated by centrifuging, washed with a little water, and finally recrystallized from hot water.



Picric acid is a crystalline solid (*m.p.* 122°). The crystals possess a bitter[1] taste and a very faint yellow colour. The acid dissolves in petroleum ether, yielding an almost colourless solution ; while the aqueous solution is deep yellow. It is a fairly strong acid, the deep yellow colour of the aqueous solution being due to the anion $C_6H_2(NO_2)_3O^-$. In acid solution, picric acid dyes wool and silk yellow. However, it is not used as a dye nowadays, as the colour is not very fast.

The chemical properties of picric acid are comparable to those of carboxylic acids. It neutralizes alkalis, yielding yellow or red coloured salts. It decomposes carbonates with the evolution of carbon dioxide. The potassium salt of picric acid is sparingly soluble, and its formation is used as a test for the potassium ion. When treated with phosphorus pentachloride, it yields **picryl chloride,** $C_6H_2(NO_2)_3Cl$, which is converted by ammonia into **picramide,** $C_6H_2(NO_2)_3NH_2$. The silver salt reacts with methyl iodide, yielding **methyl picrate** or **trinitroanisole,** $C_6H_2(NO_2)_3.OCH_3$. This possesses the properties of an ester, being saponified by hot, concentrated alkalis.

Picric acid combines with many aromatic hydrocarbons, such as naphthalene and anthracene, yielding beautifully crystalline, coloured molecular compounds. Thus **naphthalene picrate** possesses the formula $C_{10}H_8.C_6H_2(NO_2)_3OH$, and melts at 149°. The formation of such compounds is utilized in the detection and isolation of these hydrocarbons.

The most important property of picric acid is that when suddenly heated, or detonated by means of mercury fulminate, it undergoes explosive decomposition :—

$$2C_6H_2(NO_2)_3OH \rightarrow 12CO + 3N_2 + 2H_2O + H_2$$

For this reason, the compound is employed as a powerful explosive.

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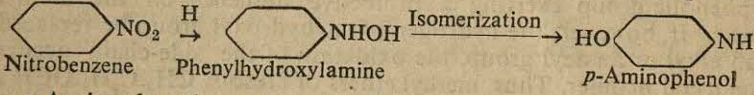
[1] Hence, the name (Gk, *pikros*, bitter).

The presence of picric acid can be detected by means of an aqueous solution of potassium cyanide, which produces a red coloration owing to the formation of *iso*-purpuric acid.

12. *p*-Aminophenol.—This compound may be obtained by the reduction of *p*-nitrophenol with iron and hydrochloric acid. It is best prepared by the electrolytic reduction of nitrobenzene in concentrated sulphuric acid solution. Phenylhydroxylamine, the first product, immediately undergoes isomerization into *p*-aminophenol :



p-Aminophenol possesses the dual character of a phenol and an amino-compound. When submitted to oxidation, it yields quinone.

Uses. (1) An alkaline solution of *p*-aminophenol, containing a small quantity of sodium sulphate, is employed as a developer in photography.

(2) Another important use of *p*-aminophenol, is in the manufacture of **phenacetin** (*p*-ethoxyacetanilide), which is obtained by acetylation of the ethyl ether of *p*-aminophenol, $NH_2C_6H_4OC_2H_5$, and is used in medicine as an antipyretic and in cases of neuralgia.

(3) It is used in dyeing hair.

13. Phenolsulphonic Acids.—When dissolved in cold, concentrated sulphuric acid, phenol yields a mixture of *o*- and *p*- **phenolsulphonic acids**, $HO.C_6H_4.SO_3H$. On heating, the ortho-compound passes into the para-compound. *p*-Phenolsulphonic acid on iodination yields **2,6-diiodo-phenol-4-sulphonic acid**, which is employed as an antiseptic under the name "**sozo-iodol**".

14. Anisole.—(phenyl methyl ether), $C_6H_5.O.CH_3$, and **phenetole** (phenyl ethyl ether), $C_6H_5.O.C_2H_5$, are both colourless liquids, (*b.p.* 155° and 172°) each possessing a characteristic odour. They resemble aliphatic ethers in chemical behaviour. When heated to a high temperature with hydrogen iodide, they get decomposed into phenol and an alkyl iodide :—

$$\underset{\text{Anisole}}{C_6H_5OCH_3} + HI \rightarrow C_6H_5OH + CH_3I$$

15. Diphenyl Ether, $C_6H_5.O.C_6H_5$, is best prepared by heating sodium phenate with bromobenzene in the presence of finely-divided copper :

$$C_6H_5ONa + Br.C_6H_5 \rightarrow C_6H_5.O.C_6H_5 + NaBr$$

It is a pleasant-smelling solid (*m.p.* 23°, *b.p.* 253°). It *differs* from alphyl aryl ethers in being not decomposed by hydrogen iodide, even at 250°.

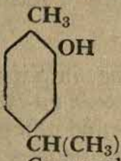
16. Homologues of Phenol.—The three hydroxytoluenes, $CH_3.C_6H_4OH$, are termed **cresols**. They are present in coal-tar, but are usually prepared from the corresponding toluidines or toluenesulphonic acids. Their respective melting and boiling points are given in the margin. Cresols resemble phenol in chemical properties, and all of them give a bluish coloration with ferric chloride.

	M.P.	B.P.
o-Cresol	30°	191°
m-Cresol	4°	203°
p-Cresol	36°	202°

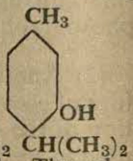
Cresols *differ* from toluene in being not oxidized by chromic acid, the phenolic group exerting a protective influence on the methyl group.[1] If, however, the hydrogen of the hydroxyl group be replaced by an alkyl or an acyl group, the oxidation of the side-chain occurs in the usual manner. Thus, methyl ethers of cresols, $CH_3.C_6H_4.OCH_3$, are readily oxidized by chromic acid to the corresponding methoxybenzoic acids, $COOH.C_6H_4.OCH_3$.

The mixture of isomeric cresols obtained from coal-tar (chap. 36, sec. 6, p. 543) is not separated, but is placed on the market as such. Being cheaper than phenol, it is much used as a disinfectant. Preparations of cresols in which the latter are brought into a soluble form by the addition of rosin-soap are sold under the name "*lysol*".

Of the other monohydric phenols, the two **hydroxy-cymenes**, known as **Carvacrol** and **Thymol**, may be mentioned. In the former, the hydroxyl group occupies the *ortho*-position with respect to the methyl group and in the latter the *meta*-position.



Carvacrol



Thymol

Carvacrol occurs in the oil of *Origanum hirtum*, and may be obtained by heating camphor with iodine :

$$C_{10}H_{16}O + I_2 \rightarrow C_{10}H_{14}O + 2HI$$

It is an oily liquid, boiling at 236°. Its alcoholic solution gives a green coloration with ferric chloride.

Thymol occurs together with cymene in oil of thyme (*ajwain*), mint and other essential oils. It is obtained from the oil of thyme by extraction with aqueous sodium hydroxide and precipitating the solution with hydrochloric acid. It crystallizes in large plates (*m.p.* 51°, *b.p.* 230°), and possesses the characteristic odour of thyme. It is only sparingly soluble in water, and gives no coloration with ferric chloride. It is a valuable antiseptic, and is used as a mouthwash, in the treatment of wounds, and for destroying intestinal worms.

17. Anethole, or *p-propenyl-anisole*, $CH_3O.C_6H_4.CH{=}CHCH_3$, is the chief constituent of aniseed oil. On oxidation, it yields **anisaldehyde**, $CH_3O.C_6H_4.CHO$, and then **anisic acid**, $CH_3.O.C_6H_4.COOH$.

II. DIHYDRIC AND TRIHYDRIC PHENOLS

18. Di- and tri-hydric phenols closely resemble monohydric phenols in most respects, but many of them are **active reducing agents** in alkaline solution. The ortho-, meta-, and para dihydric phenols show **characteristic differences** in chemical behaviour.

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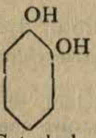
[1] Other phenols of analogous constitution behave similarly.

(1) When treated with ferric chloride, the ortho compounds usually give a green coloration and the meta-compounds a deep-violet coloration.

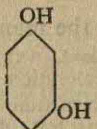
(2) The para-compounds are oxidized by ferric chloride and other oxidizing agents to quinones, which are readily recognized by their pungent odour and yellow colour.

(3) The meta-dihydric phenols, when heated with phthalic anhydride, give products that show a green fluorescence in alkaline solution (**fluorescein reaction**).

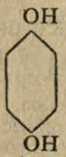
19. Dihydroxybenzenes.—The three dihydroxybenzenes are :



Catechol
(*m.p.* 104°)

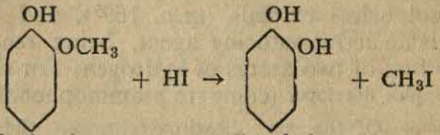


Resorcinol
(*m.p.* 119°)



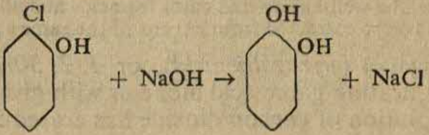
Quinol (*m.p.* 169°)

20. Catechol (*pyrocatechin*), *o-dihydroxybenzene*, occurs in catechu, a substance obtained from *Acacia catechu* and other trees. It may be obtained from phenol-*o* sulphonic acid by fusion with alkalis or from *guaiacol*, its monomethyl ether, by heating with hydriodic acid :



Guaiacol Catechol

Catechol is prepared on a commercial scale by heating, under pressure, *o*-chlorophenol with 20 per cent caustic soda solution in the presence of a little cupric sulphate (catalyst) at 190° :—



Catechol forms colourless crystals (*m.p.* 104°), readily soluble in water, alcohol, and ether. The aqueous solution gives a green coloration with ferric chloride, and precipitates metallic silver from silver nitrate solution. An alkaline solution of catechol is turned green, and finally black, by atmospheric oxidation.

Expt. 3. Properties of Catechol. (*a*) To an aqueous solution of catechol, add ferric chloride ; green colour. Add ammonia ; the colour changes to deep red.

(*b*) To an aqueous solution of catechol, add silver nitrate; black ppt. of metallic silver.

(*c*) Dissolve some catechol in a solution of sodium hydroxide. Notice the development of green colour, which gradually goes black.

21. **Resorcinol** (*resorcin*), or *m-dihydroxybenzene*, is prepared on a large scale by fusing benzene-*m*-disulphonic acid with alkali at 240° to 270°. It is also formed when *o*- or *p*- disulphonic acid and many other ortho or para di-derivatives of benzene are fused with alkali. This is due to one of the hydroxyl groups migrating to the meta position with respect to the other.

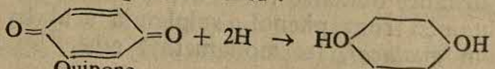
Resorcinol crystallizes in prisms or plates (*m.p.* 110°), and is readily soluble in water, alcohol, and ether. With ferric chloride, it yields deep violet coloration, and with bromine water, a crystalline precipitate of *s-tribromoresorcinol.* It gives the **flourescein reaction** (see expt. 4).

Resorcinol is much used in the manufacture of dye.

Expt. 4. Properties of Resorcinol. (*a*) Add ferric chloride to an aqueous solution of resorcinol; deep violet coloration.

(*b*) **Fluorescein reaction.** Heat a mixture of resorcinol, phthalic anhydride and some concentrated sulphuric acid in a test tube. Dissolve the product in aqueous sodium hydroxide. A brownish red solution is obtained, which, when poured into a large volume of water, shows a magnificent green fluorescence.

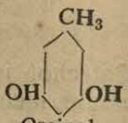
22. **Quinol** (*hydroquinone*), *p-dihydroxybenzene*, is prepared by reducing quinone with sulphurous acid :



Quinone Quinol

It forms colourless crystals (*m.p.* 169°), and is readily soluble in water. It is an active reducing agent, being readily converted into quinone by loss of two atoms of hydrogen. For this reason, it is used as a **photographic developer** (compare *p*-aminophenol).

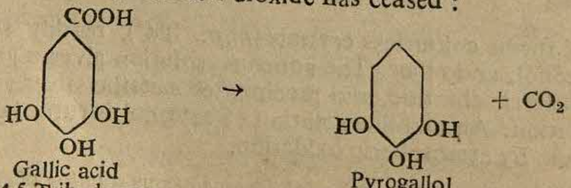
23. **Orcinol.**—Of the six dihydroxytoluenes, the 3,5-compound, called orcinol, is the best known. It may be regarded as a homologue of resorcinol, and occurs in the free state in certain lichens. It crystallizes in colourless prisms containing one molecule of water of crystallization and melting at 107°.



Orcinol

24. **Litmus**, the well-known indicator for acids and alkalis, is a derivative of orcinol. This is also extracted from lichens of the same varieties as orcinol.

25. **Pyrogallol** (*pyrogallic acid*), or *1, 2, 3-trihydroxy-benzene*, is prepared by heating gallic acid alone or with glycerol at about 210°, until the evolution of carbon dioxide has ceased :

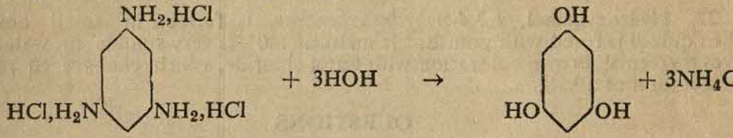


Gallic acid (3,4,5-Trihydroxy-benzoic acid)

Pyrogallol (1,2,3-Trihydroxy-benzene)

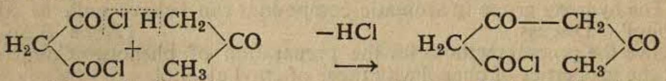
Pyrogallol forms colourless crystals (*m.p.* 132°), and is readily soluble in water. The aqueous solution gives a red coloration with ferric chloride. In alkaline solution, pyrogallol is an active reducing agent, and rapidly absorbs atmospheric oxygen, with the formation of a dark brown coloration. On this account, it is employed in gas analysis to remove oxygen from a gaseous mixture. It is also used as a developer in photography.

26 **Phloroglucinol,** *1,3,5-trihydroxybenzene*, is best prepared synthetically from 1,3,5-triaminobenzene. The hydrochloride of this base is hydrolysed by boiling with excess of water, when the amino groups get replaced by OH groups :—



Another important method of preparing phloroglucinol consists in fusing resorcinol with sodium hydroxide.

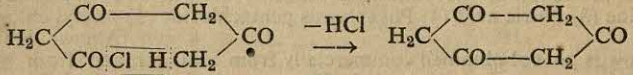
A remarkable synthesis of phloroglucinol is by the condensation of malonyl chloride with acetone. It is carried out in two steps. A mixture of the reactants in molecular proportions is first heated with calcium carbonate, the latter serving to neutralize the hydrogen chloride set free :



Malonyl chloride Acetone

Intermediate condensation product

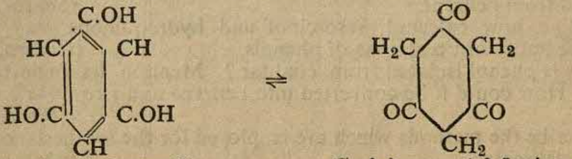
The product is then further heated with calcium carbonate and water, when phloroglucinol is produced:



Phloroglucinol (keto-form)

Phloroglucinol forms colourless crystals containing $2H_2O$, and melts at 218°. It is very soluble in water, and gives a deep violet coloration with ferric chloride. An alkaline solution of phloroglucinol, like that of pyrogallol, rapidly goes brown in air owing to absorption of oxygen.

Constitution. Phloroglucinol is a tautomeric substance :



1,3,5-Trihydroxybenzene (I) Cyclohexane-1,3,5-trione (II)

Its synthesis from malonyl chloride and acetone described above is in accord with formula II. Further, on treatment with hydroxylamine, it yields a trioxime, $C_6H_6(=NOH)_3$. On the other hand, it shows the characters of a trihydroxy compound (formula I) and gives a trimethyl ether, $C_6H_3(OCH_3)_3$, and a triacetyl derivative, $C_6H_3(O.CO.CH_3)_3$. The reaction with ferric chloride also accords with the phenolic formula.

By comparing the absorption spectra of phloroglucinol and its trimethyl ether, Hartley found that free phloroglucinol possesses the phenolic formula. The triketo form is therefore to be regarded as the labile tautomeride.

27. **Hydroxyquinol**, *1,2,4-trihydroxybenzene*, is formed in small amounts when quinol is fused with potash. It melts at 140°, is very soluble in water and gives a greenish brown coloration with ferric chloride, which changes to red on the addition of alkali.

QUESTIONS

1. Give the preparation and properties of carbolic acid. Describe a method of separating it from a sample containing acetic acid.

(*Nagpur, B.Sc., 1956*)

2. How is phenol manufactured from coal-tar? How is it purified? How would you convert it into (*a*) benzene, (*b*) salicylic acid.

(*Gauhati, B.Sc., 1957*)

3. Describe how phenol may be recovered from coal-tar. Give the action of sodium hydroxide, bromine, phosphorus pentabromide, nitric acid, sulphuric acid and acetyl chloride on phenol.

(*Jammu & Kashmir, B.Sc., 1957*)

4. 'The hydroxy group in aromatic compounds can behave both as an acid and alcohol'. Discuss.

(*Patna. B.Sc., 1958*)

5. Give the general methods for the preparation of phenols. Compare and contrast the properties of phenol with those of ethyl alcohol.

(*Osmania, B.Sc., 1959*)

6. What are phenols? How do they differ from the alcohols? How can phenol be obtained from (*i*) benzene and (*ii*) aniline? How can it be converted into (*i*) benzene and (*ii*) aniline?

What is the action of the following reagents on phenol :—(1) Caustic soda (2) Bromine (3) Nitric acid (4) Phosphorus pentachloride (5) Acetyl chloride.

(*Nagpur, B.Sc., 1960*)

7. How is phenol obtained commercially from coal tar and from benzene? By what tests would you recognise it? How can it be converted into salicylic acid and picric acid?

(*Delhi, B.Sc. 1961*)

8. How is phenol manufactured? How can it be synthesised from acetylene? Give a brief account of its properties and uses.

(*Andhra, B.Sc., 1961*)

9. How is phenol obtained commercially? In what respects it differs from an alcohol? How phenol may be converted into (*i*) picric acid (*ii*) salicylic acid?

(*Rajasthan, B.Sc., 1960*)

10. Describe the reactions of phenols (Substitution, Friedel-Craft reaction, Fries reaction, Oxidation, condensation with formaldehyde. Claisen allylation).

(*Jadavpur, B.Sc., 1961*)

11. Mention the main physical and chemical properties of phenol. How could it be derived from benzene?

(*Saugar, B.Sc., 1961*)

12. Outline how catechol, resorcinol and hydroquinone may be prepared. Describe the important reactions of phenols.

(*Andhra, B.Sc., 1961*)

13. How is phenol isolated from coal-tar? Mention its important chemical reactions. How could it be converted into benzene and *vice versa*?

(*Bihar, B.Sc., 1962*)

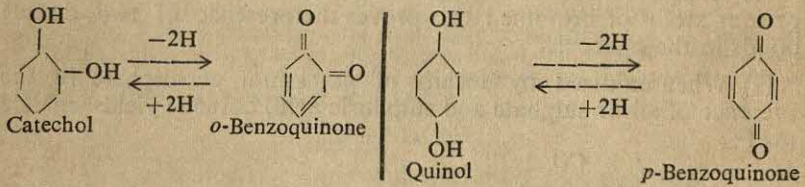
14. Describe the methods which are employed for the synthesis of Phenol on the commercial scale.

(*Lucknow, B.Sc., 1962*)

CHAPTER FORTY-EIGHT

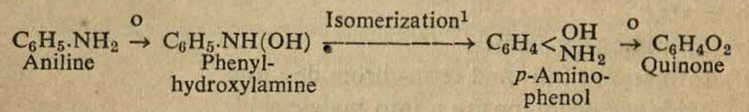
QUINONES

1. General.—Quinones are derived from ortho or para dihydric phenols by the elimination of two hydrogen atoms from the two hydroxyl groups. Thus, catechol and quinol give rise to *o*-benzoquinone and *p*-benzoquinone respectively.



No *m*-quinone has so far been isolated, and *o*-quinones of benzene hydrocarbons have only been prepared in rare cases. For this reason the *p*-compounds, which are by far the more important, are generally called *quinones*. The general methods of preparation and properties of *p*-quinones are exemplified in the following account of *p*-benzoquinone.

2. Quinone, *p-Benzoquinone*.—Quinone may be obtained by oxidizing quinol, *p*-amino-phenol, *p*-phenylenediamine, sulphanilic acid and certain other *para*-derivatives of benzene. It is generally prepared by oxidizing aniline in the cold with potassium dichromate and sulphuric acid. The reaction is supposed to take the following course :—



$$\underset{\text{Aniline}}{C_6H_5.NH_2} \xrightarrow{O} \underset{\text{Phenyl-hydroxylamine}}{C_6H_5.NH(OH)} \xrightarrow{\text{Isomerization}^1} \underset{p\text{-Amino-phenol}}{C_6H_4<^{OH}_{NH_2}} \xrightarrow{O} \underset{\text{Quinone}}{C_6H_4O_2}$$

Aniline (1 part), is dissolved in dilute sulphuric acid (concentrated acid, 8 parts and water, 30 parts), and finely powdered potassium dichromate (35 parts) is gradually added to the solution with constant stirring, the mixture being kept cool by immersion in ice-cold water. The reaction mixture, which is very dark coloured, is allowed to stand overnight in a cool place, and then extracted with ether. The ethereal layer is dried with calcium chloride, the ether is distilled off, and the crude quinone is purified by sublimation or steam-distillation.

Physical Properties.—Quinone crystallizes as golden yellow needles (*m.p.* 116°), possessing a characteristic, irritating odour. It is very volatile, and may be readily sublimed or distilled in steam. It is

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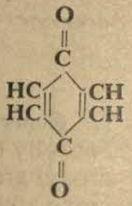
[1] Compare chap. 42, sec. 8, p. 591.

sparingly soluble in water, but dissolves freely in alcohol and ether. It colours the skin brown, and is poisonous.

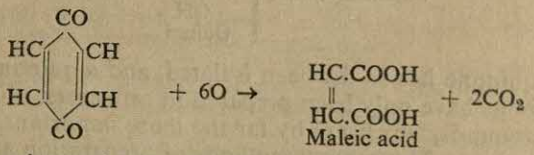
Constitution. Quinone reacts with hydroxylamine, yielding first a *monoxime*[1] and then a *dioxime*. This fact indicates the presence of two carbonyl groups in the molecule. Taking this into account, and also its formation from *para*-derivatives of benzene, quinone may be given the structure shown in the margin.



The above view is supported by the following additional facts :—

(1) In chloroform solution quinone adds on two or four atoms of bromine ; this proves the presence of two double bonds in the molecule.

(2) When oxidized by means of potassium persulphate in the presence of silver sulphate and sulphuric acid, quinone yields maleic acid :



(3) The experimental value for the parachor of quinons is 219·2, which is in very close agreement with the theoretical value (6C+4H +2O+3 double bonds + 1 six-membered ring), *i.e.*, 219·0.

From the structure of quinone, deduced above, it can be seen that quinone is *not* a substitution product of benzene. The **quinone ring is quite distinct from the benzene nucleus**, and a compound containing a quinone ring is referred to as a **quinonoid-compound**.

Chemical Properties. In addition to the properties referred to above, *viz.*,

(*i*) formation of oximes,

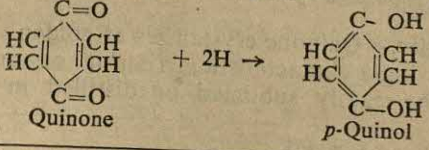
(*ii*) formation of di- and tetra- bromides, and

(*iii*) oxidative decomposition into maleic acid,

quinone shows the following reactions :—

(1) When treated with chlorine, it yields the substitution product **tetrachloroquinone**.[2]

(2) When submitted to reduction, quinone yields phenol, the **quinonoid ring passing into the benzenoid ring** :



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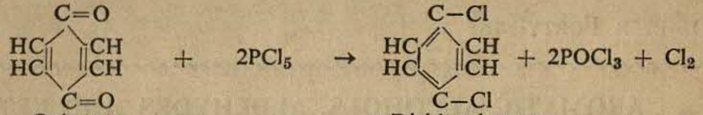
[1] This is identical with *p*-nitrosophenol (p. 640)

[2] Tetrachloroquinone, also known as **chloranil**, is employed as an oxidizing agent in the manufacture of dyes.

(3) Treatment with phosphorus pentachloride, similarly, yields *p*-dichlorobenzene :



Quinone   p-Dichlorobenzene

(4) Quinone combines with a great variety of substances, yielding addition compounds. Thus, with hydroquinone (quinol), it gives **quinhydrone**, $C_6H_4O_2$, $C_6H_4(OH)_2$.

3. ***o*-Benzoquinone** or ***o*-quinone**.—This is much less important than the *p*-compound. It is obtained by oxidizing catechol with silver-oxide. *o*-Quinone exists in two solid modifications ; the stable form crystallizes in red, transparent plates, while the unstable variety crystallizes in bright green crystals. It is colourless and non-volatile. It undergoes slow decomposition on standing, and on reduction with sulphurous acid it yields catechol.

QUESTIONS

1. What are quinones ? How are they prepared and what are their chief chemical properties ? In what important respects do *ortho-* and *para*-quinones differ from each other ?

2. Describe the preparation of quinone in the laboratory. Give its important physical and chemical properties.

3. How are quinones prepared ? In what respects do they differ from ketones ? Discuss the constitution of *p*-benzo-quinone. (*Andhra, B.Sc., 1952*)

4. What are quinones ? Describe *two* methods of preparing *p*-benzo-quinone. Discuss its important physical and chemical properties. Would you include these compounds under aromatic class ? Give reasons. (*Agra, B.Sc., 1954*)

5. Give reactions that support the formula assigned to *p*-benzoquinone. (*Punjab, B.Sc., 1960*)

6. What are quinones ? Describe two methods for preparing *p*-benzoquinone. Discuss its important chemical properties. Would you include these compounds under aromatic class ? Give reasons. (*Rajasthan, B.Sc., 1960*)

7. Write what you know of the chemistry of quinones. (*Jadavpur, B.Sc., 1960*)

CHAPTER FORTY-NINE

AROMATIC ALCOHOLS, ALDEHYDES AND KETONES

I. AROMATIC ALCOHOLS

1. Aromatic alcohols are derived from aromatic hydrocarbons by the introduction of a hydroxyl group into the side-chain. The compounds of this class differ from phenols in chemical behaviour. Both in methods of preparation and properties, they closely resemble aliphatic alcohols from which they may be regarded as derived by the replacement of a hydrogen atom of the alkyl group by an aryl group.

Benzyl alcohol (*phenylcarbinol*), $C_6H_5CH_2OH$, is a typical example of an aromatic alcohol. It occurs in the free state and as esters in many ethereal oils.

Preparation. Benzyl alcohol may be obtained by methods analogous to those used in the case of aliphatic primary alcohols. It is generally prepared in the laboratory from benzaldehyde by Cannizzaro's reaction :—

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + KOH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Potassium Benzoate}}{C_6H_5COOK}$$

The aldehyde is shaken with a cold, concentrated solution of potassium hydroxide in water, until the whole forms an emulsion. This is allowed to stand for 24 hours. Water is then added to dissolve potassium benzoate and the alcohol is extracted with ether. The ethereal layer is separated, dried and then evaporated to remove ether. The residual benzyl alcohol is purified by distillation.

Benzyl alcohol is prepared on a commercial scale by boiling benzyl chloride with milk of lime :

$$2C_6H_5CH_2Cl + Ca(OH)_2 \rightarrow 2C_6H_5CH_2OH + CaCl_2$$

Properties. Benzyl alcohol is a colourless liquid having a faint, aromatic odour and is only sparingly soluble in water. It boils at 206°. In chemical properties, it closely resembles aliphatic primary alcohols, and forms ethers and esters. When submitted to oxidation, it gives bezaldehyde, C_6H_5CHO and finally benzoic acid, C_6H_5COOH.

A point in which benzyl alcohol differs from aliphatic alcohols is, that, when treated with sulphuric acid, it is resinified and not converted into the corresponding sulphuric ester.

Benzyl alcohol entirely lacks phenolic properties, and does not dissolve in alkalis ; nor does it give any coloration with ferric chloride.

Cinnamyl alcohol, $C_6H_5.CH{=}CH.CH_2OH$, occurs as the cinnamic ester in storax. It is a crystalline substance (*m.p.* 33°) having an odour of hyacinths.

Salicyl alcohol, *o-hydroxybenzyl alcohol,* also called **saligenin** is both a primary alcohol and a phenol. It crystallizes in plates (*m.p.* 82°), is readily soluble in water and gives a deep-blue coloration with ferric chloride.

II. AROMATIC ALDEHYDES

2. Aromatic aldehydes containing the aldehyde group in the nucleus are of far greater importance than those in which this group is present in the side-chain. They differ from aliphatic aldehydes in certain important respects.

3. Methods of Formation :—

(*a*) **Methods that are common with Aliphatic Aldehydes.** The aromatic aldehydes may be prepared by methods analogous to those employed for the preparation of aliphatic aldehydes ; *e.g.*,

(1) From the corresponding primary alcohols by oxidation,

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

(2) From carboxylic acids, by distillation of the calcium salts with calcium formate,

$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} + (HCOO)_2Ca \rightarrow \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + 2CaCO_3$$

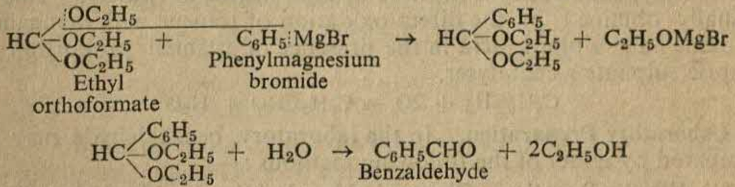
(3) From acid chlorides by Rosenmund's method :—

$$\underset{\text{Benzoyl Chloride}}{C_6H_5COCl} + H_2 \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

(4) From certain dihalogen derivatives of benzene hydrocarbons by heating with water ; *e.g.*,

$$\underset{\text{Benzal Chloride}}{C_6H_5CHCl_2} \xrightarrow{HOH} \underset{\substack{\text{unstable dihydroxy}\\\text{compound}}}{C_6H_5CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

(5) From arylmagnesium halides by treatment with ethyl orthoformate and hydrolysing the products (Reaction *iii*, p. 217).



$$\underset{\substack{\text{Ethyl}\\\text{orthoformate}}}{HC\begin{cases}OC_2H_5\\OC_2H_5\\OC_2H_5\end{cases}} + \underset{\substack{\text{Phenylmagnesium}\\\text{bromide}}}{C_6H_5MgBr} \rightarrow HC\begin{cases}C_6H_5\\OC_2H_5\\OC_2H_5\end{cases} + C_2H_5OMgBr$$

$$HC\begin{cases}C_6H_5\\OC_2H_5\\OC_2H_5\end{cases} + H_2O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + 2C_2H_5OH$$

(*b*) **Additional Methods.** The aromatic aldehydes containing the aldehyde group in direct union with the benzene nucleus may be prepared by the following methods in addition to those already described. These methods are of two types :—

(1) *Direct Introduction of the Aldehyde Group into the Benzene Ring* **(Gattermann's Synthesis).** In this method, which is really an extension of Friedel-Crafts reaction, an aromatic hydrocarbon is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride and cuprous chloride. Formyl

chloride, HCOCl, is supposed to be formed as an unstable intermediate product :

$$CO + HCl \rightarrow HCOCl$$

$$\underset{\text{Benzene}}{C_6H_6} + HCOCl \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

(2) **Oxidation of Methyl Derivatives of Benzene.** The methyl group directly attached to the benzene ring may be oxidized to a —CHO group by the following methods :

(*i*) **Etard's Reaction.** Here chromyl chloride is used as the oxidizing agent. (See under laboratory preparation of benzaldehyde).

(*ii*) By means of manganese dioxide and sulphuric acid in the presence of a little cupric sulphate as catalyst. (See under manufacture of benzaldehyde).

(*iii*) By means of aqueous lead nitrate or cupric nitrate. (See preparation of benzaldehyde from benzyl chloride).

4. **Properties.**—Aromatic aldehydes are pleasant-smelling liquids, sparingly soluble in water, but readily so in alcohol and ether. They differ from the aliphatic aldehydes in several important respects, as described under benzaldehyde.

5. **Benzaldehyde,** *Oil of Bitter Almonds*, C_6H_5CHO.—Benzaldehyde occurs in bitter almonds as the glucoside amygdalin, and was formerly obtained from this source. It may be obtained synthetically by any of the general methods described above.

Manufacture. Benzaldehyde is prepared on a large scale from toluene. Two different processes are in use :—

(1) *Through Benzal Chloride.* (Refer to chap. 41, sec. 12, p. 585).

(2) *By Direct Oxidation.* In the preparation of benzyl chloride from toluene, no matter what precautions are taken, a small amount of chlorine enters the nucleus. It is, therefore, impossible to prepare benzaldehyde free from chlorine by the above process. For use in perfumery, benzaldehyde must be of high degree of purity. This is usually obtained by the direct oxidation of toluene with manganese dioxide and sulphuric acid in the presence of a small proportion of cupric sulphate as catalyser.

$$C_6H_5CH_3 + 2O \rightarrow C_6H_5CHO + H_2O$$

Laboratory Preparation. In the laboratory, benzaldehyde may be prepared by either of the following methods :—

(1) **Etard's Reaction.** Chromyl chloride (dissolved in carbon disulphide) is gradually added to toluene (also dissolved in carbon disulphide), when a dark-coloured precipitate consisting of a molecular complex of toluene with *two* equivalents of chromyl chloride, is obtained. This is separated by filtration and then decomposed with water, when benzaldehyde, chromic chloride and chromic acid are formed :

$$C_6H_5CH_3 + 2CrO_2Cl_2 \rightarrow C_6H_5CH_3.2CrO_2Cl_2$$

$$3CrO_2Cl_2 + H_2O \rightarrow 2CrCl_3 + H_2CrO_4 + 3O$$

$$C_6H_5CH_3 + 2O \rightarrow C_6H_5CHO + H_2O$$

The chromic acid is reduced by means of SO_2 and the mixture is then steam-distilled. The bezaldehyde present in the distillate is extracted with ether. The ethereal layer is dried with calcium chloride, and distilled. The ether passes over first and then the benzaldehyde.

(2) By the oxidation of benzyl chloride with an aqueous solution of lead nitrate or of cupric nitrate (chap. 41, sec. 11, p. 585).

A mixture of benzyl chloride (1 part), water (10 parts), and lead nitrate (2 parts) is boiled under a reflux condenser, until a test-portion of the oily layer, after being thoroughly washed with water, is found to contain little or no chlorine[1]. The reaction mixture is then extracted with ether, when benzaldehyde and unchanged benzyl chloride (if any) will pass into the ethereal layer. The latter is separated, and then shaken with a concentrated solution of sodium bisulphite. The crystals of the bisulphite compound, $C_6H_5CHO.NaHSO_3$, are filtered, washed with a little ether, and then decomposed with dilute sulphuric acid. The benzaldehyde thus set free is then extracted with ether, and the ethereal layer separated, dried and distilled.

Physical Properties. Benzaldehyde is a colourless, highly refractive liquid (*b.p.* 179°) with a pleasant, characteristic odour resembling that of bitter almonds. It is sparingly soluble in water but is miscible with alcohol and ether in all proportions.

Reactions :—

(*A*) **Resemblance with Aliphatic Aldehydes.** Benzaldehyde resembles aliphatic aldehydes in the following respects :—

(1) It readily undergoes oxidation, even on exposure to air, yielding benzoic acid :

$$C_6H_5CHO + O \rightarrow C_6H_5COOH$$

It reduces ammoniacal silver solution (but not Fehling's solution).

(2) On reduction, it gives benzyl alcohol :

$$C_6H_5CHO + 2H \rightarrow C_6H_5CH_2OH$$

(3) It reacts with hydrogen cyanide and sodium bisulphite, to give a cyanohydrin and a bisulphite compound respectively.

(4) It condenses with hydroxylamine to form benzaldoxime, which exists in two stereoisomeric forms.

(5) It also condenses with phenylhydrazine to form a phenylhydrazone.

(6) It gives Schiff's reaction.

(*B*) **Distinction from Aliphatic Aldehydes.** Benzaldehyde differs from aliphatic aldehydes in the following respects :

(1) **Cannizzaro's reaction.** When boiled with alcoholic potash, benzeldehyde and its derivatives undergo **disproportionation** ; one molecule of the aldehyde being oxidized at the expense of another with the formation of sodium benzoate and benzyl alcohol (compare Formaldehyde).

$$2C_6H_5CHO + 2NaOH \rightarrow C_6H_5COONa + C_6H_5CH_2OH$$

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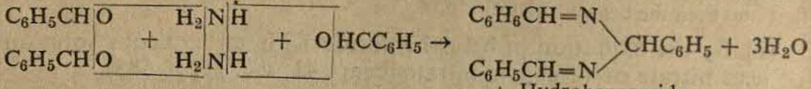
[1] This may be ascertained by boiling the sample with silver nitrate and nitric acid.

(2) **Reaction with ammonia.** Three molecules of benzaldehyde combine with two molecules of ammonia to give **hydrobenzamide** :—



$$\begin{array}{l} C_6H_5CH\,O \quad H_2N\,H \\ \qquad + \qquad\qquad\quad + \; O\,HCC_6H_5 \rightarrow \\ C_6H_5CH\,O \quad H_2N\,H \end{array} \quad \begin{array}{l} C_6H_6CH{=}N \\ \qquad\qquad \rangle CHC_6H_5 + 3H_2O \\ C_6H_5CH{=}N \end{array}$$

Hydrobenzamide

(3) **Benzoin Condensation.** When benzaldehyde is warmed with **alcoholic potassium cyanide**, two molecules condense to form a keto-alcohol, called *benzoin* :

$$C_6H_5CH{=}O + H.CO.C_6H_5 \rightarrow \underset{\text{Benzoin}}{C_6H_5CH(OH)COC_6H_5}$$

(4) Benzaldehyde condenses with certain aliphatic and aromatic compounds, with the elimination of water, yielding *unsaturated* products, *e.g.*,

(*i*) $$C_6H_5.CH\boxed{O + H_2}\underset{\text{Aniline}}{N.C_6H_5} \xrightarrow{\text{Heat}} \underset{\text{Benzylideneaniline}}{C_6H_5.CH{=}N.C_6H_5} + H_2O$$

(*ii*) $$C_6H_5CH\boxed{O + H_2}\underset{\text{Acetaldehyde}}{CH.CHO} \rightarrow \underset{\text{Cinnamaldehyde}}{C_6H_5.CH{=}CH.CHO} + H_2O$$

(*iii*) $$C_6H_5CH\boxed{O + H_2}\underset{\text{Ethyl acetate}}{CH.COOC_2H_5} \rightarrow \underset{\text{Ethyl cinnamate}}{C_6H_5.CH{=}CHCOOC_2H_5} + H_2O$$

(*iv*) $$C_6H_5CH\boxed{O + H_2}\underset{\text{Sodium acetate}}{CH.COONa} \rightarrow \underset{\text{Sodium cinnamate}}{C_6H_5{\cdot}CH{=}CH.COONa} + H_2O$$

Reaction (*ii*) and (*iii*) are examples of **Claisen's Condensation**, and are brought about in the presence of a trace of alkali. Reaction (*iv*), **Perkin's Reaction**, is discussed in detail under cinnamic acid. It is carried out by heating the substances with acetic anhydride, which serves to take up water.

(5) Benzaldehyde also readily condenses with dialkylanilines, and with phenols, to form **triphenylmethane dyes** (see chap. 51, secs. 5 and 6).

(6) Benzaldehyde may be nitrated, and sulphonated, the *m*-compounds being the principal products. Chlorination of benzaldehyde leaves the nucleus unaffected, the chlorine replacing the hydrogen of the aldehydic group with the production of benzoyl chloride :

$$C_6H_5CHO + Cl_2 \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

Tests. (1) Benzaldehyde is readily detected by its characteristic "bitter-almond" odour.

(2) On warming 0·5 ml. of benzaldehyde with 0·5 ml. of aniline and a pinch of fused zinc chloride and cooling, a white solid is deposited.

(3) On heating a mixture of benzaldehyde, dimethylaniline and fused zinc chloride, a deep green coloration is developed.

Uses. Benzaldehyde is used—

(1) In perfumery.

(2) In the manufacture of dyes.

6. Higher Homologues of Benzaldehyde and Unsaturated Aldehydes.—

Phenylacetaldehyde, $C_6H_5\,CH_2.CHO$, behaves like aliphatic aldehydes. It has an intense hyacinth-like odour, and is used in perfumery.

Cuminal, *p-Isopropyl-benzaldehyde* is present in Roman caraway oil and in the oil of water-hemlock. It boils at 235°.

Cinnamic Aldehyde, *Cinnamaldehyde,* $C_6H_5.CH{=}CH.CHO$, is the chief constituent of the oil of cinnamon, from which it may be isolated through the bisulphite compound. It is synthetically prepared by the condensation of benzaldehyde with acetaldehyde.

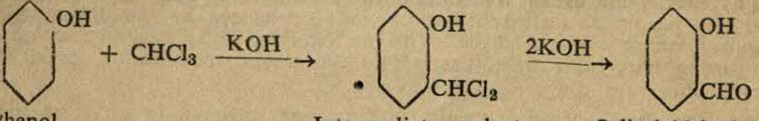
Cinnamic aldehyde is an oily liquid having an agreeable odour and boiling at 246°. On reduction with aluminium ethoxide and alcohol it gives cinnamyl alcohol; on exposure to air, it gets oxidized to cinnamic acid.

α-n-Amylcinnamic aldehyde, $C_6H_5CH{=}(C_5H_{11}).CHO$, has a strong jasamine-like odour in highly dilute solutions, and finds extensive application in synthetic perfumery.

III. PHENOLIC ALDEHYDES

7. General.—Phenolic aldehydes possess the properties of phenols, as well as of aldehydes. They may be obtained by the usual methods for preparing aromatic aldehydes.

8. Salicylaldehyde (*o-Hydroxybenzaldehyde*) is a typical example of a phenolic aldehyde. It occurs in the *oil of spiroea.* It is best prepared from phenol by the **Reimer-Tiemann reaction** which involves the direct introduction of the aldehyde group into the molecule of the phenol. A mixture of phenol, chloroform and potassium hydroxide is heated, when salicylaldehyde (together with some p-compound) is produced:—



Phenol Intermediate product Salicylaldehyde

Salicylaldehyde is separated from the p-isomer by acidifying the reaction mixture, and submitting it to steam-distillation. The salicylaldehyde passes off, leaving behind the p-isomer, which is non-volatile in steam.

Salicylaldehyde is an oily liquid (*b. p.* 196°) having a penetrating, benzaldehyde-like odour. It is moderately soluble in water, and the aqueous solution gives a deep-violet coloration with ferric chloride. When submitted to oxidation, it gives salicylic acid, and when reduced with sodium amalgam it yields salicyl alcohol.

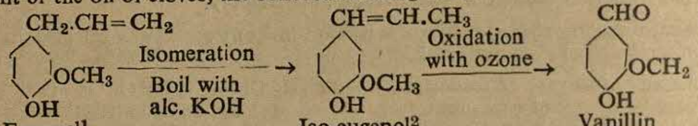
Salicylaldehyde colours the skin deep yellow, a property common to all o-hydroxyaldehydes.

Tests. 1. Salicylaldehyde smells like oil of mirbane.

2. It colours the skin yellow.

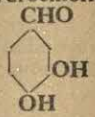
3. It is freely soluble in sodium hydroxide.
4. It gives violet coloration with ferric chloride solution.

9. **Vanillin,** *or p-Hydroxy-m-methoxy-benzaldehyde,* is the sweet smelling component of the vanilla bean. It is manufactured from *eugenol,* the chief constituent of the oil of cloves, the conversion being effected in two steps :—



Eugenol[1] Iso-eugenol[2] Vanillin

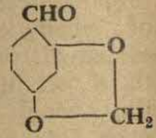
A 2·5 per cent aqueous-alcoholic solution of vanillin is much used for flavouring confectionery.



10. **Proto-catechuic Aldehyde,** *3, 4-dihydroxy benzaldehyde.*—This aldehyde was first obtained by the hydrolysis of *piperonal* by means of dilute hydrochloric acid at 200°. It is prepared from catechol by the Reimer-Triemann reaction.

Protocatechuic aldehyde is readily soluble in hot water, from which it comes out in flalt needles (*m.p.* 153°). The aqueous solution gives with ferric chloride a deep-green coloration, which changes to red on the addition of sodium carbonate (compare catechol).

Protocatechuic aldehyde possesses reducing properties, being readily oxidized to protocatechuic acid. It reduces ammoniacal silver solution.

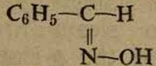


11. **Piperonal, or heliotropin**:—This is the methylene ether of protocatechuic aldehyde, from which it may be obtained by the action of methylene iodide and alkali. It has a very pleasant odour, closely resembling that of heliotropes.

Piperonal forms fine white crystals (*m.p.* 37°). It is one of the most largely used perfumes, and is employed for perfuming pomades, toilet creams, lipsalves, and soaps.

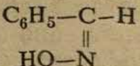
12. **Stereoisomerism of Aldoximes.**—When an aromatic aldehyde is treated with hydroxylamine, usually a mixture of two aldoximes is obtained. In certain cases, only one oxime (called the α-compound) is produced by the direct action of hydroxylamine on the aldehyde. This, on treatment with a mineral acid, or in exposure to ultra-violet light, passes into the second modification, called the β-compound.

The two forms of an aromatic aldoxime are believed to be geometrical isomers ; one of them possessing the *syn-* and the other the *anti-* formula :



$$\begin{array}{c}C_6H_5\text{—}C\text{—}H\\ \|\\ N\text{—}OH\end{array}$$

syn-Benzaldoxime
(m.p. 35°)



$$\begin{array}{c}C_6H_5\text{—}C\text{—}H\\ \|\\ HO\text{—}N\end{array}$$

anti-Benzaldoxime
(m.p. 125°)

IV. AROMATIC KETONES

13. **General.**—There exist (*i*) purely aromatic ketones, such as benzophenone, $C_6H_5.CO.C_6H_5$, and (*ii*) mixed alphyl aryl ketones, *e.g.*, acetophenone, $C_9H_5.CO.CH_3$. Both the classes closely resemble the aliphatic ketones in properties.

Aromatic ketones may be prepared by methods similar to those used for aliphatic ketones. A special method of preparing aromatic ketones is by the interaction of benzene hydrocarbons and acid chlorides in the presence of anhydrous aluminium chloride (**Friedel and Crafts' reaction**).

---

[1] *p*-Hydroxy-*m*-methoxy-allylbenzene.

[2] *p*-Hydroxy-*m*-methoxy-propenylbenzene.

$$C_6H_6 + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \rightarrow \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$$

14. Acetophenone, *methyl phenyl ketone*, $C_6H_5COCH_3$.—This is the best known of the alphyl aryl ketones. It may be prepared—

(1) By distilling an equimolecular mixture of calcium benzoate and calcium acetate :

$$(C_6H_5COO)_2Ca + (CH_3COO)_2Ca \rightarrow 2C_6H_5COCH_3 + 2CaCO_3$$

(2) By dropping acetyl chloride into well-cooled benzene, in the presence of anhydrous aluminium chloride (Friedel and Crafts' reaction) :

$$C_6H_6 + Cl.CO.CH_3 \rightarrow C_6H_5COCH_3 + HCl$$

Properties. Acetophenone is a crystalline solid (*m.p.* 20°, *b.p.* 202°), having a fragrant odour. It is slightly soluble in water.

In chemical behaviour, acetophenone is very similar to acetone. Thus, on reduction with sodium amalgam and aqueous alcohol, it yields methyl-phenylcarbinol.

$$C_6H_5.CO.CH_3 + 2H \rightarrow C_6H_5.CHOH.CH_3$$

On oxidation, the aliphatic side-chain gets oxidized to carboxyl group with the production of benzoic acid :

$$C_6H_5.CO.CH_3 + 4O \rightarrow C_6H_5COOH + CO_2 + H_2O$$

Further, it reacts with hydrogen cyanide, hydroxylamine and phenylhydrazine.

However, acetophenone *does not combine with sodium bisulphite*. This is **characteristic of all ketones having carbonyl in direct union with cenzene ring.**

Acetophenone, of course, differs from aliphatic ketones in the fact that, as an aromatic compound, it can be nitrated and sulphonated[1].

Use. Acetophenone is used as a *hypnotic* in medicine, under the name of **hypnone.**

15. Benzophenone, *Diphenyl Ketone*, $C_6H_5.CO.C_6H_5$.—This compound may be obtained by the usual methods, and is most easily prepared from benzene by Friedel and Crafts' reaction :

$$C_6H_6 + \underset{\text{Benzoyl chloride}}{C_6H_5.COCl} \rightarrow C_6H_5.CO.C_6H_5 + HCl$$

$$2C_6H_6 + \underset{\text{Carbonyl chloride}}{COCl_2} \rightarrow C_6H_5.CO\ C_6H_5 + 2HCl$$

Benzophenone exists in two modifications, an unstable form, melting at 27°, and a stable form, melting at 49°. The conversion of the unstable into the stable modification is a non-reversible process (*monotropy*).

Benzophenone possesses the usual properties of a ketone, and reacts with hydrogen cyanide, hydroxylamine, phenyldrazine, etc., in exactly the same manner as aliphatic ketones. When subjected to reduction, it yields the secondary alcohol diphenylcarbinol or

---

[1] **On chlorination, however, it gives $C_6H_5.CO.CH_2Cl$.**

benzhydrol $(C_6H_5)_2CHOH$, and finally **diphenylmethane**,[1] $(C_6H_5)_2CH_2$. When fused with potassium hydroxide, it undergoes decomposition, yielding benzoic acid and benzene :

$$\begin{array}{l} C_6H_5CO{:}C_6H_5 \rightarrow C_6H_5COOK + C_6H_6 \\ \quad + KOH \end{array}$$

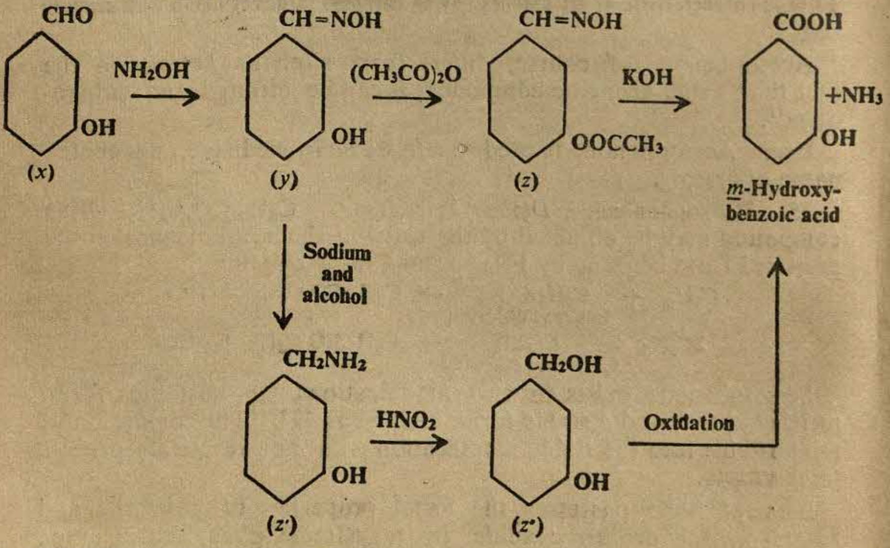
16. Michler's ketone, *p, p'-bisdimethylaminobenzophenone,* $(CH_3)_2N\langle\overline{\quad}\rangle{-}CO{-}\langle\overline{\quad}\rangle N(CH_3)_2$, is prepared by the action of carbonyl chloride on dimethylaniline. Michler's ketone and the secondary alcohol derived from it are both employed commercially in the **Manufacture of triphenylmethane dyes.**

17. Stereoisomerism of Ketoximes.—Symmetrical ketones, *e.g*,, benzophenone, $C_6H_5.CO.C_6H_5$, give rise to only *one* ketoxime, but unsymmetrical ketones, such as pheny-tolylketone, $C_6H_5.CO.C_6H_4CH_3$, and monochlorobenzophenone, $C_6H_5CO.C_6H_4Cl$, yield two different oximes, which, like the aldoximes, are geometrical isomers.

Problem. An organic compound (*x*), containing C, 68.84%, H, 4.92%, and O, 26.24% and with a vapour density of 61, reacts with hydroxylamine to give a compound (*y*), which on treatment with acetic anhydride gives another compound (*z*). The compound (*z*) when reacted with KOH gives ammonia and *m*-hydroxy-banzoic acid. Again, the compound (*y*) when treated with sodium and alcohol gives a compound (*z'*) which with nitrous acid gives another one (*z''*). The compound (*z''*) on oxidation gives *m*-hydroxybenzoic acid. Name all the five compounds, and explain the above changes. (*Banaras, B.Sc., 1953*)

The molecular formula of the compound *x*, calculated in the usual manner, is $C_7H_6O_2$.

Examination of the molecular formula, coupled with the fact that *m*-hydroxybenzoic acid is one of the products of the series of reactions indicated in the problem, reveals that the compound *x* is a derivative of benzene, C_6H_6. Since there are *two* atoms of oxygen in the molecule, *x* may be either benzoic acid, C_6H_5COOH or a hydroxybenzaldehyde, $C_6H_4(OH)CHO$, obviously the *meta*-compound. This view is fully supported by the series of reactions given in the problem, as shown below :—



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[1] The first stage of the reaction is carried out by means of sodium amalgam and the second by distillation with zinc-dust.

Hence, the five compounds are :
x is *m*-Hydroxybenzaldehyde
y is *m*-Hydroxybenzaldoxime
z is *m*-Acetylhydroxybenzaldoxime
z′ is *m*-Hydroxybenzylamine
z″ is *m*-Hydroxybenzyl alcohol.

Note. Hydrolysis of aldoximes in a hot alkaline solution has been observed (Jordan and Hauser, 1936) to give the carboxylic acid, probably through the formation of nitrile followed by hydrolysis :

$$RCH{=}NOH \xrightarrow{KOH} RCN \xrightarrow{HOH} RCOOH + NH_3$$

QUESTIONS

1. How is benzaldehyde prepared commercially ? Compare its properties with those of acetaldehyde. What are its more important uses ? (*Agra, B.Sc., 1956*)

2. How is benzaldehyde manufactured ? What is the action of benzaldehyde on (*a*) hydrogen cyanide, (*b*) potassium cyanide, (*c*) dimethyl aniline, (*d*) caustic soda, (*e*) ammonia ? (*Rangoon, B.Sc., 1956*)

3. How would you convert benzene into benzaldehyde ? In what respects does it differ from and resemble aliphatic aldehydes ? How do you account for the white deposit observed round the stopper of the laboratory bottle of benzaldehyde ? (*Bihar, B.Sc. 1955*)

4. How is benzaldehyde manufactured ? Compare and contrast its properties with those of acetaldehyde. (*Osmania, B.Sc., 1956*)

5. An organic liquid is shaken with caustic potash, until the reaction is complete, when two organic substances may be isolated from the reaction products. One is of the composition C, 77·8 : H, 7·4 and O, 14·8 per cent and when oxidized yields the original substance. The other substance is the potassium salt of an acid, and when heated with lime, yields an aromatic hydrocarbon. Discuss these reactions. (*Calcutta, B.Sc., 1934*)

(*Ans.* Original substance was benzaldehyde ; the products of the reaction were benzyl alcohol and potassium benzoate.)

6. Write short notes on *any three* of the following :—
(*a*) Friedel and Crafts' reaction.
(*b*) Rosenmund reaction.
(*c*) Claisen condensation.
(*d*) Perkin's reaction.
(*e*) Stephen's reaction.
(*f*) Gattermann synthesis.
(*Lucknow, B.Sc., 1962*)

7. In what important chemical properties do aromatic compounds differ from the corresponding aliphatic compounds ? Illustrate your answer by taking examples of chlorobenzene, phenol, aniline and benzaldehyde. (*Lucknow, B.Sc., 1960*)

8. Give a detailed account of the general methods of preparing phenolic aldehydes. Discuss the properties of salicyladehyde. (*Lucknow, B.Sc., 1959*)

9. Give the synthesis of ortho-hydroxybenzaldehyde. (*Lucknow, B.Sc., 1961*)

10. How is benzaldehyde prepared ? Give its important reactions and show how it differs from acetaldehyde. (*Jabalpur, B.Sc., 1960*)

11. Give two important methods of obtaining salicylaldehyde. Compare and contrast its reactions with those of benzaldehyde. (*Punjab, B.Sc., 1961*)

12. Give an account of the preparation and properties of phenolic aldehydes and ketones. (*Annamalai, B.Sc., 1961*)

13. Give two important methods of obtaining salicylaldehyde. Compare and contrast its reactions with those of benzaldehyde. (*Punjab, B.Sc., 1961*)

14. Describe giving equations, the preparation, properties and uses of salicylaldehyde. (*Calcutta, B.Sc., 1962*)

15. An organic liquid when shaken with a strong solution of KOH gave two substances, *A* and *B*. *A* contained 77.8% carbon, 7.4% hydrogen, and the rest oxygen. *A* on oxidation gave back the original substance. *B* is the potassium salt of an acid which when heated with soda-lime gave aromatic hydrocarbon. Discuss the reactions. What is the main reaction called ? (*Poona, B.Sc., 1954*)

Ans. The main reaction is called *Cannizzaro's reaction.* The given liquid is benzaldehyde ; *A* is benzyl alcohol and *B* potassium benzoate.

CHAPTER FIFTY

AROMATIC ACIDS

I. MONOBASIC ACIDS WITH CARBOXYL GROUP IN NUCLEUS

1. General Methods of Preparation.—

(*A*) These acids may be obtained by the usual methods for preparing aliphatic carboxylic acids ; *e.g.*,

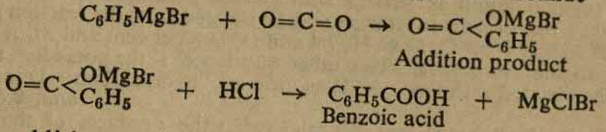
(1) *By the Oxidation of a Primary Alcohol, or an Aldehyde* :

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + 2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(2) *From the corresponding Halogen Derivative through the Grignard Reaction* :

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + Mg \rightarrow \underset{\text{Phenylmagnesium bromide}}{C_6H_5MgBr}$$



$$C_6H_5MgBr + O{=}C{=}O \rightarrow \underset{\text{Addition product}}{O{=}C{<}\begin{matrix}OMgBr\\ C_6H_5\end{matrix}}$$

$$O{=}C{<}\begin{matrix}OMgBr\\ C_6H_5\end{matrix} + HCl \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + MgClBr$$

(*B*) In addition to the above, the following **additional methods** are available for preparing the aromatic acids containing the COOH group in direct union with the benzene nucleus :—

(1) *Direct Introduction of a Carboxyl Group into Benzene Nucleus* (**Friedel and Crafts' Reaction**). When a benzene hydrocarbon is treated with carbonyl chloride, in the presence of anhydrous aluminium chloride, we get an acid chloride, which, on treatment with water, gives the corresponding acid ; *e.g.*,

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Carbonyl chloride}}{Cl.CO.Cl} \xrightarrow{(+\ AlCl_3)} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

$$C_6H_5COCl + H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$$

(2) *By Oxidation of a Side-chain*. The oxidation of a homologue of benzene (or of a derivative containing a substituted side-chain) is the most important method of preparing aromatic acids. The aliphatic side-chain, whatever its length, is oxidized to a carboxyl group. The oxidation is carried out by means of dilute nitric acid or potassium permanganate in alkaline solution :

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

(3) **From an Amino Compound through Sandmeyer's Reaction :—**

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{\text{Diazotize}} \underset{\substack{\text{Benzene-}\\ \text{diazonium chloride}}}{C_6H_5N_2Cl} \xrightarrow{CuCN} \underset{\text{Benzonitrile}}{C_6H_5CN} \xrightarrow{HOH} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(4) **From a Sulphonic Acid.** When the potassium salt of an aromatic sulphonic acid is fused with potassium cyanide, we get a nitrile, which, on hydrolysis, gives an aromatic acid :

$$\underset{\substack{\text{Potassium benzene-}\\ \text{sulphonate}}}{C_6H_5SO_3K} \xrightarrow{KCN} \underset{\text{Benzo-nitrile}}{C_6H_5CN} \xrightarrow{HOH} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

An alternative method consists in fusing alkali salts of sulphonic acids with sodium formate.

2. General Properties.—Aromatic carboxylic acids are colourless, crystalline solids, readily soluble in hot water, less so in the cold. In general chemical behaviour, they resemble the aliphatic acids. On account of the electronegative nature of the benzene nucleus, the aromatic acids are stronger electrolytes than the aliphatic acids. Further, like aromatic hydrocarbons, they may be converted into the chloro-, nitro-, amino- and other derivatives.

3. Benzoic Acid, C_6H_5COOH.

Occurrence.—(1) Benzoic acid occurs in the free state in gum-benzoin and in the balsams of Peru and Tolu.

(2) In the form of hippuric acid (benzoylglycine, $C_6H_5.CO.NH.CH_2COOH$), it is present in the urine of the horse.

Preparation. (1) Benzoic acid is obtained on the commercial scale from toluene. The latter substance is first chlorinated at its boiling-point to give benzotrichloride, which is then hydrolysed with milk of lime :—

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{Cl_2} C_6H_5CCl_3 \xrightarrow{HOH} \underset{\text{(unstable)}}{C_6H_5C(OH)_3} \xrightarrow{-H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

The calcium salt of benzoic acid thus obtained is treated with hydrochloric acid, when benzoic acid is precipitated. The acid is purified by crystallization from hot water.

(2) Much benzoic acid is also prepared commercially from naphthalene *via* phthalic acid (sec. 7). The latter substance is partially decarboxylated by cautiously heating with soda-lime :

$$C_6H_5(COONa)_2 + NaOH \rightarrow C_6H_5COONa + Na_2CO_3$$

(3) In the laboratory, the acid may be conveniently prepared by the oxidation of benzyl chloride by means of an alkaline solution of potassium permanganate :—

$$\begin{array}{rr} 2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O & [\times 2] \\ \underline{C_6H_5CH_2Cl + 2KOH + 2O \rightarrow C_6H_5COOK + KCl + 2H_2O} & \underline{[\times 3]} \\ 3C_6H_5CH_2Cl + 4KMnO_4 + 2KOH \rightarrow 3C_6H_5COOK + 3KCl + 4MnO_2 + 4H_2O & \end{array}$$

The excess alkali required in the reaction is added in the form of sodium carbonate.

In a one-litre flask, provided with reflux condenser (Fig. 1) are placed benzyl chloride (1 part) and a solution of Na_2CO_3 (1 part), in water (10 parts). The mixture is gently boiled and the calculated amount of potassium permanganate (8 parts) dissolved in water (30 parts) is added gradually from a dropping funnel pushed down the top of the condenser. The boiling is continued, until the pink colour of the permanganate has disappeared. The liquid is allowed to cool to about 80°, and a current of sulphur dioxide is passed into it, until the precipitate of manganese dioxide has completely dissolved. On allowing the reaction mixture to cool, crystals of benzoic acid separate out. These are filtered off, washed with a small quantity of cold water, and finally recrystallized from hot water.

(3) For pharmaceutical purposes, benzoic acid is still obtained from gumbenoin by sublimation.

Properties. Benzoic acid forms colourless, glistening plates (*m.p.* 121°, *b.p.* 250°), and has a faint aromatic odour. It is readily soluble in hot water, alcohol and ether. It sublimes readily, and is volatile in steam; the vapour has an irritating action on the nose and the throat, and causes violent coughing.

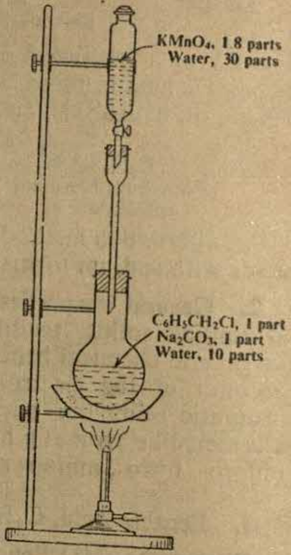


Fig. 1. Preparation of Benzoic acid from Benzyl chloride.

Benzoic acid has the usual properties of a carboxylic acid. It forms salts, esters, benzoyl chloride, benzoic anhydride and benzamide. When distilled with soda-lime, it yields benzene. Further, like other aromatic compounds, it may be chlorinated, nitrated or sulphonated, the meta-compound being the main product in each case.

Expt. 1. Tests of Benzoic Acid. (1) Warm sodium benzoate with concentrated sulphuric acid; evolution of irritating vapour.

(2) Warm some benzoic acid or sodium benzoate with soda-lime; evolution of combustible vapour of benzene.

(3) To a *neutral* solution of a benzoate, add ferric chloride; light-brown precipitate of ferric benzoate.

Uses. Benzoic acid is used—

(*i*) in medicine, and

(*ii*) in the manufacture of dyes.

4. Benzoic Acid Derivatives.—

Ethyl benzoate, $C_6H_5COOC_2H_5$. This ester is prepared by the Fischer-Speier method. It consists in boiling benzoic acid with twice its weight of absolute alcohol in the presence of a little concentrated sulphuric acid or anhydrous hydrogen chloride, which act as catalysts:

$$C_6H_5COOH + C_2H_5OH \rightleftharpoons C_6H_5COOC_2H_5 + H_2O$$

Expt. 2. Preparation of Ethyl Benzoate :—

Benzoic acid, 50 gm.
Ethyl alcohol, 100 gm. (125 ml.)
Concentrated sulphuric acid, 10 gm. (5·4 ml.)

Place the mixture in a round-bottom flask, provided with a reflux condenser, and boil it for three hours. Distil off the greater part of alcohol and pour the residue into about five times its volume of the cold water, neutralize the liquid with solid sodium carbonate, and extract the oily ester with ether. Separate the ethereal layer, and dry it over fused calcium chloride. Decant the clear liquid into a distillation flask and distil off the ether. Replace the water condenser by an air condenser, and distil off ethyl benzoate, catching the fraction passing over at 205°—215° in a clean dry receiver.

Ethyl benzoate has a pleasant, aromatic odour, and boils at 213°. It closely resembles ethyl acetate in chemical properties.

Benzoyl Chloride, C_6H_5COCl, is obtained by distilling benzoic acid with phosphorus pentachloride :

$$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + POCl_3 + HCl$$

It is also prepared commercially from benzal chloride. The latter substance on hydrolysis yields benzaldehyde, which on chlorination gives benzoyl chloride.

$$C_6H_5CHCl_2 + 2HOH \rightarrow C_6H_5CHO + 2HCl$$
$$C_6H_5CHO + Cl_2 \rightarrow C_6H_5COCl + HCl$$

Benzoyl chloride is a colourless oily liquid, with an extremely irritating odour. In chemical behaviour, benzoyl chloride is analogous to acetyl chloride. Thus, it is decomposed by water, though far more slowly than acetyl chloride yielding benzoic acid and hydrochloric acid.

Use. Benzoyl chloride is frequently employed for introducing the benzoyl group, $C_6H_5CO—$, into hydroxy-, amino-, and imino-compounds. The process is known as **benzoylation**, and is carried out by shaking the compound to be benzoylated with an excess of benzoyl chloride and dilute sodium hydroxide solution, **(Schotten-Baumann reaction)**.

$$(i)\ C_6H_5O\boxed{H + Cl}COC_6H_5 \rightleftharpoons \underset{\text{Phenyl benzoate}}{C_6H_5COOC_6H_5} + HCl$$

$$(ii)\ \underset{\text{Aniline}}{C_6H_5NH_2} + C_6H_5COCl \rightleftharpoons \underset{\text{Benzanilide}}{C_6H_5NHCOC_6H_5} + HCl$$

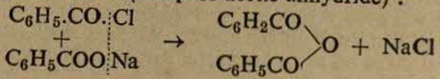
The alkali serves to remove the hydrochloric acid as soon as formed, and thus prevents the reaction from being reversed. The benzoyl derivative is separated by filtration or extraction with ether, and is then purified. Since benzoyl derivatives crystallize much more readily than the corresponding acetyl derivatives, they are prepared in preference to the latter for the *identification or isolation of hydroxy and amino compounds.*

Expt. 3. Benzoylation of Aniline.

Aniline, 2 gm.
Benzoyl chloride, 2 ml.
Sodium hydroxide solution (10 per cent), 10 ml.

Place aniline[1] and sodium hydroxide solution in a small flask, and warm the latter on a water-bath. Add benzoyl chloride gradually to the warm mixture with continued shaking. Loosely cork the flask, and shake the contents vigorously for a few minutes. If the smell of benzoyl chloride still persists, destroy it by warming with a further quantity of sodium hydroxide solution. Pour the contents of the flask into water, when benzanilide will separate out as a precipitate. Filter the latter, wash with water, dry and recrystallize from alcohol (*m.p.* 161°—162°).

Benzoic anhydride, $(C_6H_5CO)_2O$, is obtained by the interaction of benzoyl chloride and sodium benzoate (compare acetic anhydride) :



$$\begin{matrix} C_6H_5.CO.\vdots Cl \\ + \\ C_6H_5COO\vdots Na \end{matrix} \rightarrow \begin{matrix} C_6H_2CO \\ C_6H_5CO \end{matrix}\!\!>O + NaCl$$

It is a crystalline substance, closely resembling acetic anhydride in chemical behaviour. Like benzoyl chloride, it is employed for the **benzoylation** of hydroxy and amino compounds.

Benzamide, $C_6H_5CONH_2$, is obtained by the action of ammonia or ammonium carbonate on benzoyl chloride or ethyl benzoate :

$$C_6H_5COCl + NH_3 \rightarrow C_6H_5CONH_2 + HCl$$

$$C_6H_5COOC_2H_5 + NH_3 \rightarrow C_6H_5CONH_2 + C_2H_5OH$$

Expt. 4. Preparation of Benzamide :

Ammonium carbonate 10 gm.

Benzoyl chloride, 5 gm. (4·1 ml.)

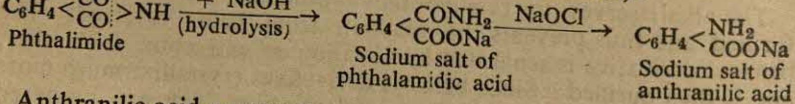
Place the finely powdered ammonium carbonate in a mortar, add benzoyl-chloride from a burette, and thoroughly rub the mixture with a pestle. If the smell of benzoyl chloride persists even after ten minutes, add a few drops of concentrated ammonia to complete the reaction. Treat the product with water to dissolve out the ammonium chloride. Filter the solid benzamide at the pump, and wash with *cold* water. Recrystallize from hot water, and dry the crystals on a porous plate.

Benzamide is a colourless, crystalline solid, readily soluble in hot water. It is similar to acetamide in chemical properties, and when boiled with alkalis it gives ammonia and the alkali benzoate :

$$C_6H_5CONH_2 + KOH \rightarrow C_6H_5COOK + NH_3$$

5. Substituted Benzoic Acids.—

Anthranilic acid, *o-Aminobenzoic acid,* $C_6H_4<^{NH_2}_{COOH}$. This acid was first obtained by the oxidation of indigo. It is of great importance as **an intermediate in the production of synthetic indigo,** and is manufactured on a large scale from phthalimide by the action of sodium hyprochlorite and sodium hydroxide (**Hofmann's Reaction**) :



$$C_6H_4<^{CO}_{CO}>NH \xrightarrow[\text{(hydrolysis)}]{+\ NaOH} C_6H_4<^{CONH_2}_{COONa} \xrightarrow{NaOCl} C_6H_4<^{NH_2}_{COONa}$$

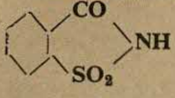
Phthalimide; Sodium salt of phthalamidic acid; Sodium salt of anthranilic acid

Anthranilic acid possesses a sweet taste, and melts at 145°. By the action of gentle heat, it may be sublimed without decomposition, but stronger heating decomposes it into carbon dioxide and aniline.

---

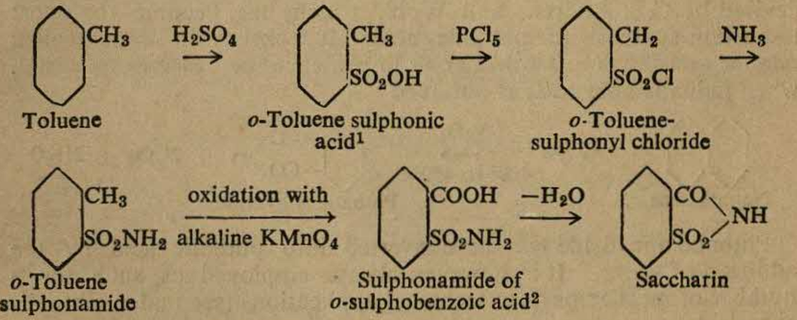
[1] If the compound to be benzoylated is solid, it should be *finely powdered* beforehand.

Sulphobenzoic acids, $C_6H_4<\substack{COOH\\SO_2OH}$ (*o*-, *m*-, and *p*-), are obtained from the corresponding toluene-sulphonic acids, by oxidation. Direct sulphonation of benzoic acid yields *m*-sulphobenzoic acid as the chief product.



Saccharin, the cyclic imide of *n*-sulphobenzoic acid, is about 500 times as sweet as cane-sugar, and is used as a substitute for cane-sugar in diabetes. It is also used as a sweetening agent in tooth-pastes, aerated waters, etc. It has, however, no nutritive value.

Saccharin is **manufactured from toluene** by the following series of reactions :



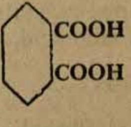
CH₃
H₂SO₄
Toluene
CH₃
SO₂OH
o-Toluene sulphonic acid¹
PCl₅
CH₂
SO₂Cl
o-Toluene-sulphonyl chloride
NH₃
CH₃
SO₂NH₂
o-Toluene sulphonamide
oxidation with alkaline KMnO₄
COOH
SO₂NH₂
Sulphonamide of o-sulphobenzoic acid²
−H₂O
CO
NH
SO₂
Saccharin

Saccharin is only slightly soluble in water ; hence it is put on the market in the form of its **sodium salt,** $C_6H_4<\substack{CO\\SO_2}>NNa$, which is readily soluble, and is about 400 times as sweet as sugar.

6. **Toluic Acids,** $C_6H_4<\substack{CH_3\\COOH}$.—The *o*-, *m*- and *p*-toluic acids (*m.p.* 105°, 111° and 180°) may be obtained by the partial oxidation of the corresponding xylenes by means of dilute nitric acid. They closely resemble benzoic acid in properties. On oxidation, they are converted into the corresponding *phthalic acids*, $C_6H_4(COOH)_2$,

II. DIBASIC ACIDS WITH CARBOXYL GROUPS IN NUCLEUS

7. **Phthalic Acid,** *Benzene-o-dicarboxylic Acid.*—Of the three-benzene-dicarboxylic acids, the ortho-compound is the most important.



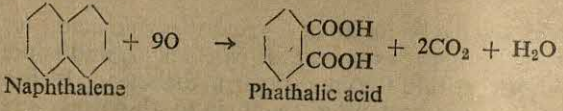
Phthalic acid was first prepared by its discoverer Laurent, in 1836, by the oxidation of 1,2,3,4-tertrachloronaphthalene with nitric acid.

---

[1] The sulphonation of toluene yields, of course, a *mixture* of the *o*- and *p*-sulphonic acids. These are separated at the **sulphonyl chloride** stage by mixing the product with ice, and filtering, when the *o*-compound filters through as an oily liquid, while the *p*-compound, being solid at that temperature, remains on the filter.

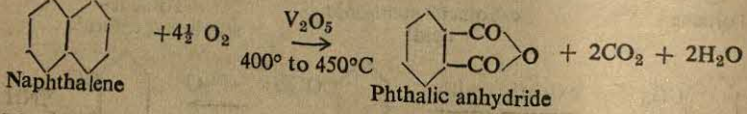
[2] On the liberation of this acid from its alkali salt, by means of sulphuric acid, a molecule of water is at once eliminated with the formation of saccharin.

Uptil recently, phthalic acid was commercially prepared by the **Badische process**, which consisted in the oxidation of naphthalene with fuming sulphuric acid in the presence of mercuric sulphate as catalyser :



During the oxidation, the sulphur trioxide present in the acid, got reduced to sulphur dioxide.

The Badische process has now been replaced by a **new process**, devised by C.E. Andrens and Wohl, which has become the most important synthesis of phthalic acid. It consists in a controlled **catalytic oxidation of naphthalene by air** in presence of **vanadium pentoxide**, when **phthalic anhydride** is obtained :—



Phthalic anhydride may be converted into phthalic acid by the addition of water. It is, however, always employed as such for a number of most important technical applications (see under phthalic anhydride).

Phthalic acid is a colourless, crystalline substance, which melts at 184°, yielding the anhydride. If the melted substance be allowed to solidify, and its melting-point redetermined, it will be found to be 128°, the melting-point of the anhydride.

Test. Both phthalic acid and the anhydride can be readily identified by the **fluorescein reaction** (p. 646, Expt. 4(*b*)).

Phthalic Anhydride. This substance has become a **most important intermediate.** It is prepared on a very large scale from naphthalenes as described above.

Properties. Phthalic anhydride sublimes forming long, needle-shaped crystals (*m.p.* 128°C). It slowly combines with water to form phthalic acid.

Uses.—

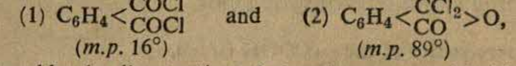
(1) Phthalic anhydride is employed directly in the synthesis of many dyes of rhodamine and fluorescein series.

(2) It is even of greater value as a step in the manufacture of anthraquinone and its derivatives, in which direction it has opened up the entire field of anthraquino vat-dyes at very reasonable prices.

(3) Large quantities of phthalic anhydride are now also consumed in making resins and plasticizers.

8. Phthalic Acid Derivatives.—

Phthalyl chloride exists in two tautomeric forms :—



$$(1)\ \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{COCl}}{\mathrm{COCl}} \quad \text{and} \quad (2)\ \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CCl_2}}{\mathrm{CO}}>\mathrm{O},$$

(*m.p.* 16°) (*m.p.* 89°)

The first is produced by the direct action of phosphorus pentachloride on phthalic anhydride. It passes into the second form when warmed with aluminium chloride. The two forms show physical and chemical differences. Thus, when treated with guaiacol and acenaphthene, the symmetrical form yields a greenish-yellow solution while the unsymmetrical form remains colourless.

Phthalimide, $\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{NH}$, (*m.p.* 238°), is obtained by passing dry ammonia over heated phthalic anhydride. When an alcoholic solution of phthalimide is treated with potassium hydroxide, a precipitate of **potassium phthalimide,** $\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{NK}$, is formed.

Phthalimide is employed in the synthesis of anthranilic acid while potassium phthalimide has been employed for the synthesis of *primary amines* and primary amino-compounds with a great variety of substituents (**Gabriel's phthalimide reaction**).

III. PHENOLIC ACIDS

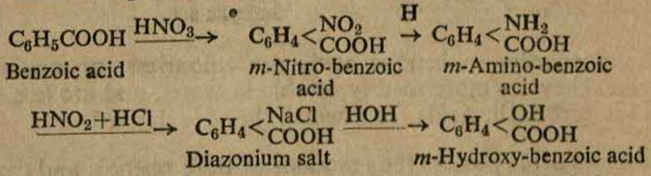
Phenolic acids are derived from the aromatic carboxylic acids by the replacement of *nuclear* hydrogen by one or more hydroxyl groups. They possess the dual character of a phenol and a carboxylic acid.

9. Methods of Formation.—The general methods for the preparation of phenolic acids may be divided into two groups :

(*A*) **By introduction of the OH group into the molecule of an aromatic carboxylic acid.—**

This may be accomplished in either of the following ways :—

(1) By the *nitration* of the carboxylic acid, followed by the reduction of the nitro-acid to the amino-acid. The latter is then diazotized and the diazo-compound heated with water :



$$\mathrm{C_6H_5COOH} \xrightarrow{\mathrm{HNO_3}} \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{NO_2}}{\mathrm{COOH}} \xrightarrow{\mathrm{H}} \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{COOH}}$$

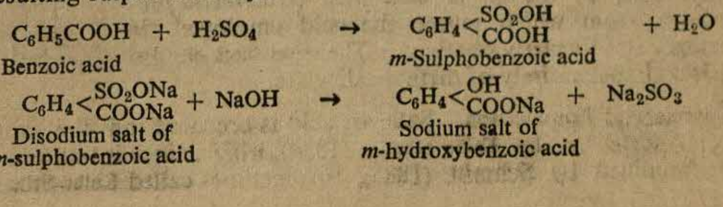
Benzoic acid *m*-Nitro-benzoic acid *m*-Amino-benzoic acid

$$\xrightarrow{\mathrm{HNO_2+HCl}} \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{NaCl}}{\mathrm{COOH}} \xrightarrow{\mathrm{HOH}} \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{COOH}}$$

Diazonium salt *m*-Hydroxy-benzoic acid

The *o*- and *p*-phenolic acids may of course be obtained from the corresponding amino-carboxylic acids through the diazo-reaction.

(2) By the *sulphonation* of the carboxylic acid and fusing the resulting sulpho-carboxylic acid with sodium hydroxide :



$$\mathrm{C_6H_5COOH} + \mathrm{H_2SO_4} \rightarrow \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{SO_2OH}}{\mathrm{COOH}} + \mathrm{H_2O}$$

Benzoic acid *m*-Sulphobenzoic acid

$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{SO_2ONa}}{\mathrm{COONa}} + \mathrm{NaOH} \rightarrow \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{COONa}} + \mathrm{Na_2SO_3}$$

Disodium salt of *m*-sulphobenzoic acid Sodium salt of *m*-hydroxybenzoic acid

The *o*- and *p*-phenolic acids may similarly be obtained from the corresponding sulpho-carboxylic acids.

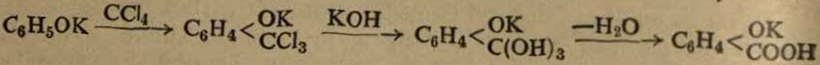
(*B*) **By introduction of the —COOH Group.—**

Of the following methods, the first two involve the direct introduction of the —COOH group into the molecule of a phenol, while the third is based on the oxidation of a $—CH_2OH$ or —CHO group.

(1) By heating the dry sodium salt of a phenol with carbon dioxide under pressure (see under salicylic acid).

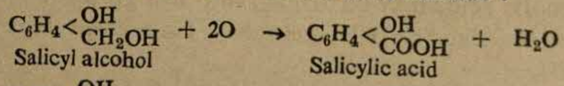
Di- and trihydric phenols may be converted into phenolic acids simply by heating them with ammonium carbonate or potassium bicarbonate.

(2) By boiling a strongly alkaline solution of a phenol with carbon tetrachloride, a mixture of *o*-and *p*-phenolic acid is formed. The reaction may be assumed to take the following course compare Reimer-Tiemann reaction for the preparation of phenolic a.dehydes:—



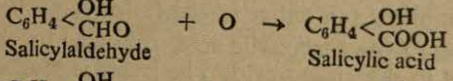
$$C_6H_5OK \xrightarrow{CCl_4} C_6H_4<^{OK}_{CCl_3} \xrightarrow{KOH} C_6H_4<^{OK}_{C(OH)_3} \xrightarrow{-H_2O} C_6H_4<^{OK}_{COOH}$$

(3) By the oxidation of phenolic alcohols and phenolic aldehydes by means of chromic acid, or of phenols having an aliphatic side-chain by fusion with caustic alkali and lead dioxide :



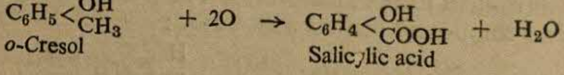
$$C_6H_4<^{OH}_{CH_2OH} + 2O \rightarrow C_6H_4<^{OH}_{COOH} + H_2O$$

Salicyl alcohol Salicylic acid



$$C_6H_4<^{OH}_{CHO} + O \rightarrow C_6H_4<^{OH}_{COOH}$$

Salicylaldehyde Salicylic acid



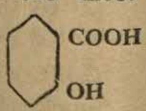
$$C_6H_5<^{OH}_{CH_3} + 2O \rightarrow C_6H_4<^{OH}_{COOH} + H_2O$$

o-Cresol Salicylic acid

10. Properties.—Phenolic acids are colourless, crystalline substances. They are more readily soluble in water, and are less volatile, than the carboxylic acids from which they are derived.

Phenolic acids possess the reactions of both phenols and carboxylic acids, as exemplified below in the case of salicylic acid.

11. Salicylic Acid. *o-Hydroxybenzoic acid.*—This is the most important of the monohydroxy acids. It occurs as the methyl ester in the **oil of wintergreen** (*Gaultheria procumbens*), from which source the acid employed in pharmacy was formerly obtained. The **sweet-birch oil** also consists almost entirely of methyl salicylate.



Commercial Preparation. Salicylic acid is prepared on the commercial scale by the **Kolbe reaction** (1874), which, since it was somewhat modified by Schmitt (1885), is sometimes called **Kolbe-Schmitt**

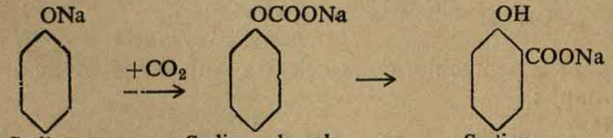
reaction.[1] The starting material in the process is phenol, which is run into a hot aqueous solution of sodium hydroxide in a heated iron tank, when sodium phenate is produced,

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \longrightarrow \underset{\text{Sodium phenate}}{C_6H_5ONa} + H_2O$$

The solution of sodium phenate, thus obtained, is transferred to autoclaves provided with stirrers, and there evaporated to complete dryness in vacuum at 130°. The temperature is then reduced to 100°, and dry carbon dioxide gas is introduced under 6 atmosphere pressure.

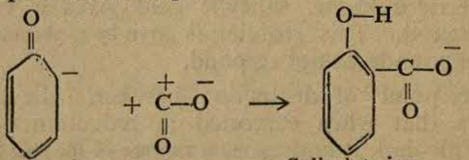
The product is dissolved in water, and the solution, after being decolorized with activated carbon, is acidified with excess hydrochloric acid, when salicylic acid is precipitated. This is further purified by recrystallization from hot water.

Mechanism of the Reaction. The mechanism of the Kolbe-Schmitt reaction is still uncertain. According to Schmitt, the carbon dioxide is absorbed by sodium phenate to form, in the first instance, sodium phenyl carbonate. The —COONa group then exchanges place with one of the activated *ortho* hydrogen atoms to produce sodium salicylate :—



Sodium phenate   Sodium phenyl carbonate   Sodium salicylate

According to the modern theory of aromatic substitution (chapter 40), the reaction is most simply explained by assuming that the anion of phenol having a partial negative charge on the *ortho*-carbon atom (p. 577) reacts as a nucleophilic reagent directly with carbon dioxide in its dipolar form to produce the salicylate anion :—



Phenolate ion   Salicylate ion

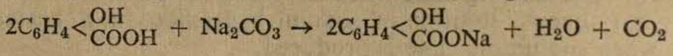
Physical Properties. Salicylic acid forms colourless needles (*m. p.* 155°). It is sparingly soluble in cold water, but readily so in hot water, alcohol, or chloroform.

Reactions. Salicylic acid combines the properties of a carboxylic acid and a phenol.

---

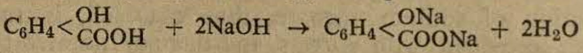
[1] In the original Kolbe procedure, sodium phenate was heated with carbon dioxide, under pressure, at 180° to 200°C. Under these conditions, however, only one-half of the phenate ion was utilized. Schmitt's improvement of the process consists in operating at a lower reaction temperature (130° to 140°) for a longer period, which prevents the loss of phenol that the original process involved.

(1) When treated with an alkali carbonate, a *mono-metallic salt* is formed by the replacement of carboxylic hydrogen :



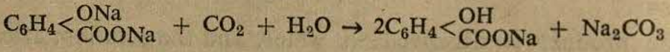
$$2C_6H_4<\substack{OH\\COOH} + Na_2CO_3 \rightarrow 2C_6H_4<\substack{OH\\COONa} + H_2O + CO_2$$

An alkali hydroxide, on the other hand, replaces both the phenolic and the carboxylic hydrogen atoms, yielding a *dimetallic derivative* :



$$C_6H_4<\substack{OH\\COOH} + 2NaOH \rightarrow C_6H_4<\substack{ONa\\COONa} + 2H_2O$$

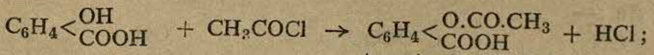
The dimetallic salts are decomposed by carbon dioxide with the formation of mono-metallic salts :



$$C_6H_4<\substack{ONa\\COONa} + CO_2 + H_2O \rightarrow 2C_6H_4<\substack{OH\\COONa} + Na_2CO_3$$

(2) On treatment with an alcohol and gaseous hydrogen chloride, it forms an *ester*, such as ethyl salicylate, $C_6H_4(OH)COOC_2H_5$. The ester reacts with a cold solution of an alkali, yielding a metallic derivative, such as $C_6H_4(ONa)COOC_2H_5$. When heated with an alkyl halide, the metallic derivative yields an *alkyl derivative* of the type $C_6H_4(OCH_3)COOC_2H_5$.

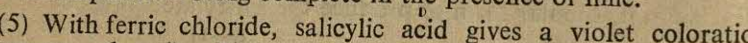
(3) Acetyl chloride replaces the phenolic hydrogen by an acetyl group,



$$C_6H_4<\substack{OH\\COOH} + CH_3COCl \rightarrow C_6H_4<\substack{O.CO.CH_3\\COOH} + HCl\,;$$

Acetyl-salicylic acid

while phosphorus pentachloride attacks on both the phenolic and the carboxyl groups :



$$C_6H_4<\substack{OH\\COOH_5} + 2PCl_5 \rightarrow CH_4<\substack{Cl\\COCl} + 2POCl_3 + 2HCl$$

o-Chlorobenzene chloride

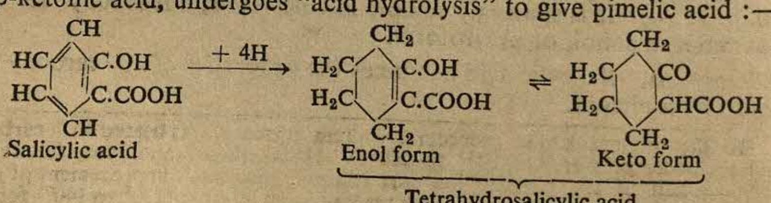
(4) When heated, salicylic acid partly sublimes and partly undergoes decomposition into phenol and carbon dioxide,

$$C_6H_4(OH)COOH \rightarrow C_6H_5OH + CO_2,$$

the decomposition being complete in the presence of lime.

(5) With ferric chloride, salicylic acid gives a violet coloration (compare phenol). This reaction is **given by *o*-phenolic acids only** ; the *m*- and *p*-compounds do not respond.

(6) Another point of distinction between salicylic acid and its isomerides is that when subjected to reduction with sodium and boiling amyl alcohol, it undergoes a **rapture of the ring** to form pimelic acid. The reaction occurs through the intermediate formation of **tetrahydrosalicylic acid.** The keto form of the latter acid, being a β-ketonic acid, undergoes "acid hydrolysis" to give pimelic acid :—

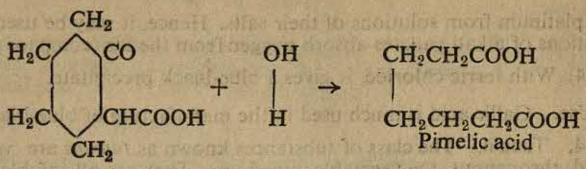


Salicylic acid

Enol form

Keto form

Tetrahydrosalicylic acid



When salicylic acid is boiled with a solution of calcium chloride and ammonia, it yields a precipitate of monocalcium salicylate, $(C_6H_4(OH)COO)_2Ca$. This reaction affords a means of **separating salicylic acid from its isomerides,** which do *not* give insoluble calcium salts.

12. Salicylic Acid Derivatives.—

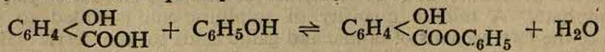
Sodium salicylate, $C_6H_4(OH)COONa$, is prepared by neutralising the acid with sodium carbonate. It forms colourless, pearly scales having a sweetish taste. It is used in medicine.

Methyl salicylate, $C_6H_4(OH)COOCH_3$, as already mentioned, is the chief constituent of **oil of wintergreen** and **sweet birch oil.** It is prepared artificially on a large scale by saturating a solution of salicylic acid in methyl alcohol with gaseous hydrogen chloride. It boils at 224°.

Uses. (1) Methyl salicylate is much used in dental preparations, and is a constituent of synthetic acacia and other flower oils.

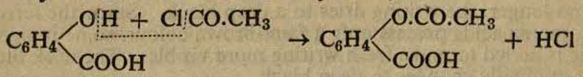
(2) It is also used as un anti-rheumatic.

Phenyl salicylate, $C_6H_5(OH)COOC_6H_5$, (*m.p.* 42°) is known as **salol,** and is used as an antiseptic. It is prepared by the interaction of phenol and salicylic acid in the presence of an acid chloride, such as carbonyl chloride or phosphorus oxychloride.[1]



$$C_6H_4{<}^{OH}_{COOH} + C_6H_5OH \rightleftharpoons C_6H_4{<}^{OH}_{COOC_6H_5} + H_2O$$

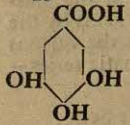
Acetylsalicylic acid, (*m.p.* 128°) is prepared by heating salicylic acid with acetyl chloride or acetic anhydride,



$$C_6H_4{<}^{O|H\ +\ Cl|CO.CH_3}_{COOH} \rightarrow C_6H_4{<}^{O.CO.CH_3}_{COOH} + HCl$$

and is used medicinally in cases of rheumatism under the name **"aspirin".**

13. Galic acid ; *3, 4, 5-Trihydroxybenzoic acid,* is the most important of the six possible trihydroxy benzoic acids. It occurs in gall-nuts, tea, root of the pomegranate, and "divi-divi" a material used in tanning. It is generally prepared by boiling *tannin* with dilute acids. The product is extracted with ether, in which the tannin is insoluble and is, therefore, left in the aqueous layer.



Properties. (1) Gallic acid is readily soluble in alcohol, ether, or boiling water, and crystallizes from the latter solvent with 1 H_2O.

(2) When heated to about 220°, it decomposes into pyrogallol and carbon dioxide.

(3) Gallic acid possesses reducing properties, and precipitates gold, silver,

---

[1] The acid chloride serves to eliminate water and thus help esterification.

and platinum from solutions of their salts. Hence, it may be used in photography. Solutions of alkali gallates absorb oxygen from the air (compare pyrogallol).

(4) With ferric chloride, it gives a blue-black precipitate.

Use. Gallic acid is much used in the manufacture of blue-black ink.

14. Tannin.—The class of substances known as *tannins* are very widely distributed throughout the vegetable kingdom. They are all soluble in water, possess a bitter, astringent taste, yield dark blue or green precipitates with ferric salts, and precipitate proteins from their solutions. By virtue of the last named property, they are largely used in the **manufacture of leather** from animal hides.

From the chemical standpoint, tannins fall into a number of quite different groups. The group that has been best investigated includes the tannin of the tannic acid class. These may be described as esters formed by the combination of phenolic acids with sugars.

15. Tannic Acid.—Tannic acid, also known as **gallotannic acid**, is the typical and most important tannin. It is present to the extent of 50 per cent in gall-nuts; and also occurs in tea, sumach and other plants. It is best separated by extracting finely powdered gall-nuts with an ether-alcohol mixture. The product obtained is a mixture and not a pure chemical individual.

Tannic acid is a colourless, amorphous substance, readily soluble in water and sparingly so in alcohol and ether. The aqueous solution possesses the properties typical of tannins.

Uses. (1) Tannic acid is used as a reagent for proteins and alkaloids.

(2) It is employed in medicine as an active astringent and haemostatic.

(3) It is employed as a mordant for basic dyes.

(4) The most important commercial use of tannic acid is in the tanning of leather.

(5) In common with gallic acid, tannic acid finds application in the manufacture of ink.

(6) Tannic acid has also been used for the clarification of wine.

16. Blue-Black Ink.—Ordinary blue-black ink consists of a solution containing a mixture of tannic and gallic acids (or aqueous extract of gall-nuts) with ferrous sulphate. A minute quantity of sulphuric acid is added to retard the oxidation of the ferrous salts of tannic and gallic acids to the ferric salts, which, being insoluble, would give a thick black precipitate. A little phenol is also added to prevent mouldiness. When used for writing, the acidity of the ink gets neutralized by the aluminium oxide present in the paper and oxidation being prevented no longer, the writing dries to a deep black. Since the ferrous salts of gallic and tannic acids possess only a faint-brown colour, some indigo-carmine or aniline-blue is added to make fresh writing more visible. The dark blue colour of the writing gradually changes to deep black.

IV. ARYL-SUBSTITUTED ALIPHATIC ACIDS

17. General.—The aromatic acids containing the carboxyl group in the *side-chain* may be regarded as derived from the aliphatic carboxylic acids by the replacement of hydrogen of the aliphatic chain by aryl groups. Thus, the various series of aliphatic carboxylic acids have their counterparts in the aromatic series—

Aliphatic Acids	Counterpart in the Aromatic Series
Acetic Acid, CH_3COOH	Phenylacetic acid, $C_6H_5CH_2COOH$
Propionic acid, CH_3CH_2COOH	Phenylpropionic acid, $C_6H_5CH_2CH_2COOH$
Acrylic acid, $CH_2{=}CH.COOH$	Phenylacrylic acid, $C_6H_5CH{=}CH.COOH$
Propiolic acid, $CH{\equiv}C.COOH$	Phenylpropiolic acid, $C_6H_5.C{\equiv}C.COOH$

The aryl substituted aliphatic acids resemble the corresponding aliphatic compounds in their methods of preparation and chemical behaviour. Further, they posses the usual reactions of the aromatic nucleus.

18. Aryl-Aliphatic Saturated Acids.—

Phenylacetic acid, $C_6H_5CH_2COOH$, is prepared from benzyl chloride by the following series of reactions :

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{KCN} \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN} \xrightarrow{HOH} \underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH}$$

It crystallizes from water in glistening plates having a characteristic odour and melting at 76°. When oxidized with chromic acid, it yields benzoic acid.

Mandelic Acid, *phenylhydroxyacetic acid*, $C_6H_5.CH(OH).COOH$, contains an asymmetric carbon atom, and consequently exists in two optically active forms and an inactive racemic form. The latter is prepared from benzaldehyde as shown below.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{+\ HCN} \underset{\text{Mandelonitrile}}{C_6H_5CH(OH)CN} \xrightarrow{HOH} \underset{\text{Mandelic acid}}{C_6H_5CH(OH)COOH}$$

It may be resolved into the *d*- and *l*- forms by the recrystallization of the cinchonine salts, the one derived from the *d*-acid crystallizing first. *l*-Mandelic acid may also be obtained directly by boiling amygdalin (which is a natural glucoside of benzaldehyde cyanohydrin) with hydrochloric acid.

Synthetic mandelic acid melts at 118°, while each of the optically active forms melts at 135°.

In chemical behaviour, mandelic acid closely resembles aliphatic hydroxy acids. Thus, when heated with hydriodic acid, it is reduced to phenylacetic acid, $C_6H_5.CH_2.COOH$. When carefully oxidized, it yields benzoylformic acid, $C_6H_5.CO.COOH$; vigorous oxidation results in the formation of benzoic acid, C_6H_5COOH.

19. Cinnamic Acid.—$C_6H_5.CH{=}CH.COOH$, β-*Phenylacrylic Acid*.

This is the most important unsaturated acid of the aromatic series. It occurs free or as esters in the balsams of Peru and Tolu and in storax (a resin obtained from *Styrax officinalis*) :

Preparation :—

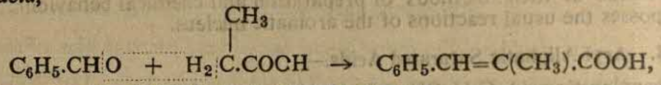
(1) **Perkin's Synthesis.** The most important method for the preparation of cinnamic acid consists in condensing benzaldehyde with sodium acetate in the presence of acetic anhydride. The process has been shown by Fittig to proceed in two stages analogous to the formation of aldol and crotonaldehyde from acetaldehyde :

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{+\ CH_3COONa} \underset{\substack{\text{Intermediate addition}\\ \text{compound (hypothetical)}}}{C_6H_5.CH(OH).CH_2.COONa}$$

$$\xrightarrow{-H_2O} \underset{\text{Sodium cinnamate}}{C_6H_5.CH{=}CH.COONa}$$

Perkin's synthesis is of a very general application, since benzaldehyde may be replaced by its homologues, its halogen or nitro substitution products, etc., and, instead of sodium acetate, sodium salts of other fatty acids, halogen-substituted acids, and dibasic acids of the succinic series may be used. In this manner, numerous acids and their substituted derivatives can be obtained.

It has been shown that in Perkin's reaction the aldehydic carbon atom always links itself to the α-carbon. Thus, benzaldehyde and propionic acid give *α-methyl-cinnamic acid*,



$$C_6H_5.CHO + H_2\overset{\overset{CH_3}{|}}{C}.COOH \rightarrow C_6H_5.CH{=}C(CH_3).COOH,$$

and *not* the isomeric acid $C_6H_5.CH{=}CH.CH_2.COOH$.

(2) **Claisen's Condensation.** This consists in condensing benzaldehyde with ethyl acetate in the presence of sodium ethoxide :

$$\underset{\text{Ethyl acetate}}{C_6H_5.CHO + H_2CH.COOC_2H_5} \rightarrow \underset{\text{Ethyl cinnamate}}{C_6H_5CH{=}CH.COOC_2H_5} + H_2O$$

Claisen's reaction, too, is of general application.

Manufacture. Cinnamic acid is prepared on a commercial scale by heating benzal chloride with sodium acetate :

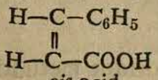
$$C_6H_5CHCl_2 + H_2CH.COONa \rightarrow C_6H_5CH{=}CHCOOH + NaCl + HCl$$

Properties. Cinnamic acid crystallizes from hot water in needles (*m.p.* 133°, *b.p.* 300°). It has a sweet odour, and is used in perfumery in blending with certain types of rose and similar perfumes.

(2) It possesses the usual properties of an ethylenic compound, and combines directly with hydrogen, bromine, and hydrogen bromide, yielding phenylpropionic acid (hydrocinnamic acid), α, β-dibromophenylpropionic acid, $C_6H_5.CHBr.CHBr.COOH$ and β-bromo-phenylpropionic acid[1], $C_6H_5.CHBr.CH_2.COOH$, respectively. It decolorizes Baeyer's reagent. When distilled with lime, it yields the unsaturated hydrocarbon, styrene, $C_6H_5.CH{=}CH_2$.

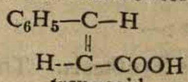
(3) Like other aromatic derivatives, cinnamic acid can be readily nitrated. when it gives a mixture of about equal quantities of *o-* and *p- nitrocinnamic acids*. On oxidation, it yields benzoic acid.

Isomerism. Cinnamic acid exists in two stereoisomeric forms :



$$\begin{matrix} H{-}C{-}C_6H_5 \\ \| \\ H{-}C{-}COOH \end{matrix}$$

cis-acid



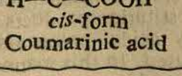
$$\begin{matrix} C_6H_5{-}C{-}H \\ \| \\ H{-}C{-}COOH \end{matrix}$$

trans-acid

Ordinary cinnamic acid is supposed to be the trans-compound, and melts at 133°. The other isomeride, the cis-form, exhibits the unusual phenomenon of **trimorphism**, *i.e.*, it exists in three different crystalline modifications (melting-points 68°, 58° and 42°), which are inter-convertible.

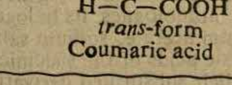
20. ***o*-Hydroxycinnamic Acid,** $C_6H_4{<}\begin{matrix}CH{=}CHCOOH\\OH\end{matrix}$

Like cinnamic acid, this acid occurs in two stereoisomeric forms :



$$\begin{matrix} H{-}C{-}C_6H_4.OH \\ \| \\ H{-}C{-}COOH \end{matrix}$$

cis-form
Coumarinic acid



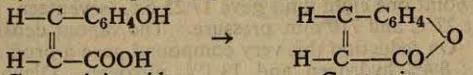
$$\begin{matrix} HO.C_6H_4{-}C{-}H \\ \| \\ H{-}C{-}COOH \end{matrix}$$

trans-form
Coumaric acid

---

[1] Compare acrylic acid.

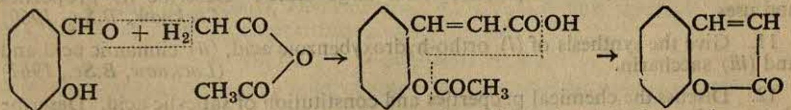
Coumarinic acid. The *cis*-form of *o*-hydroxycinnamic acid is stable only in the form of its salts. When set free by the addition of mineral acid to a solution of one of its salts, it at once passes into its anhydride, called *coumarin*,



$$\begin{matrix}H-C-C_6H_4OH\\ \Vert\\ H-C-COOH\end{matrix} \rightarrow \begin{matrix}H-C-C_6H_4\diagdown\\ \Vert \qquad\qquad O\\ H-C-\!\!-CO\diagup\end{matrix}$$

Coumarinic acid Coumarin

Coumarin, the anhydride of coumarinic acid, is responsible for the sweet odour of woodruff (*Asperula odorata*) and of Tonka bean. It is prepared by heating salicylaldehyde with sodium acetate and acetic anhydride (**Perkin's reaction**). The first product of the reaction is acetylcoumaric acid, which, by the action of heat, loses a molecule of acetic acid and passes into coumarin :



Salicylaldehyde Acetylcoumaric acid Coumarin

Coumarin is a white crystalline solid (*m.p.* 68°, *b.p.* 300°), sparingly soluble in cold water. It is much used in perfumery ; being very volatile, it requires a good fixative.

QUESTIONS

1. How would you proceed to introduce the COOH group into the benzene ring ? (*Punjab, B.Sc., 1930*)

2. How is salicylic acid prepared ? What are its important reactions and uses ? (*Rajputana, B.Sc., 1952*)

3. How is cinnamic acid prepared ? Give two examples of the general nature of the reaction involved in its formation. By what chemical tests would you distinguish between benzoic acid, cinnamic acid and salicylic acid ? (*Andhra, B.Sc., 1952*)

4. How would you prepare saccharin from toluene. (*Punjab, B.Sc., 1950*)

5. What is mandelic acid ? How can this be prepared ? What are its properties ? Compare mandelic acid with lactic acid so far as the action of (*i*) HNO_3, (*ii*) HI, (*iii*) HCl on both these compounds is concerned. (*Nagpur, B.Sc., 1945*)

6. An organic acid gave on analysis the following figures :—0·1606 gm. gave 0·3146 gm. CO_2 and 0·532 gm. H_2O. In an analysis of the silver salt 0·1915 gm. gave 0·114 gm. silver. When oxidized with nitric acid, the acid yielded a new acid containing 47·2 per cent of carbon and 2·3 per cent of hydrogen ; whilst, when distilled with lime, it yielded toluene. Discuss the possible constitution of the acid. (*Punjab, B.Sc., Hons., 1923*)

7. 0·174 gm. of an organic amino acid gave on combustion 0·392 gm. of CO_2 and 0·0795 gm. of H_2O. 0·30 gm. of the substance gave 24·57 ml. of N_2 at 0°C and 740 mm. When diazotized, treated with potassium cyanide, and hydrolysed, it gave an acid whose silver salt contained 56·84 per cent of silver. This acid, when heated, yields an anhydride. Discuss the constitution of the amino-acid. (*Punjab, B.Sc., 1931*)

8. A substance (*A*) has the following percentage composition : C, 70·6%, H, 5·9% and O, 23·53%. Its vapour density is 68. The substance (*A*) when treated with PCl_5 and subsequently with NH_3 gives a substance *B*. *B*, when treated with bromine and caustic potash, forms a base *C* which on diazotization and boiling with water gives *o*-cresol. What are *A*, *B* and *C* ? (*Banaras, B.Sc., 1952*)

Ans. (*A*) is *o*-toluic acid, $C_6H_4{<}\begin{matrix}CH_3\\COOH\end{matrix}$, (*B*) its amide and (*C*) *o* toluidine.

9. The nitro derivative of an aromatic hydrocarbon gave the following results on analysis. 0·28 gm. (point two eight gm.) gave 0·629 gm. (point six two nine gm.) of carbon dioxide and 0·129 gm. (point one two nine gm.) of water. Further 0·18 gm. (point one eight gm.) gave 17·25 c.c. (seventeen point two five c.c.) of nitrogen at 27°C and 710 mm. pressure. The vapour density of the nitro-derivative is 68·5. On reduction this very compound gave a product [B] containing 78·5% carbon ; 8·4% hydrogen and 13·1% nitrogen. Diazotisation of [B] and subsequent treatment by the sandmeyer's reaction employing potassium cyanide and cuprous cyanide gave a product C_8H_7N. Also [B] gave an acetyl derivative [C] which contains 9·4% nitrogen. [C] on oxidation and hydrolysis gave anthranilic acid. Assign constitutional formula to the original nitro derivative and explain the reactions. (*Rajasthan, B.Sc., 1960*)

10. How is salicylic acid prepared on a large scale ? Describe its properties and uses. (*Lucknow, B.Sc., 1960*)

11. Give the synthesis of (*i*) ortho-hydroxybenzoic acid, (*ii*) cinnamic acid and (*iii*) saccharin. (*Lucknow, B.Sc., 1961*)

12. Discuss the chemical properties and constitution of salicylic acid. Describe the manufacture of the salicylic acid, and give the preparation of any *two* of its derivatives which are useful as drugs. (*Bombay, B.Sc., Chemistry, Subs., 1962*)

13. How is phthalic acid manufactured ? Illustrate with equations the synthetic use of its anhydride. (*Gujarat, B.Sc., 1957*)

14. Write a note on Kolbe-Schmitt reaction. (*Punjab, B.Sc., 1963*)

CHAPTER FIFTY-ONE

POLYPHENYL COMPOUNDS

In this chapter the compounds containing two or more benzene nuclei united either directly or through one or more carbon atoms, will be discussed.

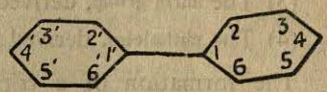
1. **Diphenyl** or **Biphenyl**, *Phenylbenzene*, $C_6H_5C_6H_5$—This hydrocarbon may be obtained by passing benzene through a red-hot tube :

$$2C_6H_6 \rightarrow C_6H_5.C_6H_5 + H_2$$

It is best prepared by heating iodobenzene with finely-divided copper at 220° :

$$2C_6H_5I + 2Cu \rightarrow C_6H_5.C_6H_5 + 2CuI$$

Diphenyl forms colourless crystals (*m.p.* 70°), and is readily soluble in alcohol and ether. It possesses an aromatic character, and can be readily nitrated or halogenated, the substituents entering the para- and the ortho- positions by preference (Crum-Brown rule). Oxidation converts it into benzoic acid, one of the rings being destroyed.



The position of substituents in the diphenyl molecule is denoted by numerals as shown in the margin :

Of the derivatives of diphenyl, the following two may be mentioned. **Benzidine** or 4, 4'-*diaminodiphenyl*, which is obtained by intramolecular rearrangement of hydrazobenzene is an important dye-stuffs intermediate and is used in the manufacture of azo-dyes. **Diphenic acid** is *diphenyl-2,2'-dicarboxylic acid*, and is of interest in connection with the structure of phenanthrene.

2. **Diphenylmethane**, *benzylbenzene*, $C_6H_5.CH_2.C_6H_5$.—This hydrocarbon may be prepared by the action of benzyl chloride on benzene, in the presence of anhydrous aluminium chloride (*Friedel and Crafts' reaction*) :

$$C_6H_5CH_2\boxed{Cl + H}C_6H_5 \rightarrow C_6H_5.CH_2.C_6H_5 + HCl$$

Diphenylmethane forms needle-shaped crystals having an **odour of oranges** and melting at 26°. When treated with nitric acid, it gives nitro derivatives, and when oxidized with chromic acid, it is converted into benzophenone, $C_6H_5.CO.C_6H_5$.

3. **Triphenylmethane**, $(C_6H_5)_3CH$.—The derivatives of this hydrocarbon are of great importance, since they include widely used **dye-stuff and indicators.** Triphenylmethane may be readily obtained by the action of benzal chloride, or of chloroform, on benzene in the presence of anhydrous aluminium chloride (*Friedel and Crafts' reaction*) :

$$C_6H_5.CHCl_2 + 2H.C_6H_5 \rightarrow (C_6H_5)_3CH + 2HCl$$
$$CHCl_3 + 3H.C_6H_5 \rightarrow (C_6H_5)_3CH + 3HCl$$

Triphenylmethane forms colourless prisms. It melts at 93° and boils at 359°. It is soluble in benzene, ether and hot alcohol.

The **hydrogen atom of the methane residue** in triphenylmethane is **very reactive**. On being oxidized with chromic acid, the hydrocarbon yields *triphenylcarbinol*, $(C_6H_5)_3COH$.

Triphenylmethane can be readily nitrated, one nitro group entering each ring in the para-position.

4. Triphenylmethane Dyes.—Triphenylmethane dyes are intermediate between the extremely numerous, cheap azo-dyes and the comparatively small class of vat dyes. The following are the chief groups of this class of dyes :

(1) The **malachite green group,** derived from diaminotriphenylmethane.

(2) The **resaniline group,** derived from triaminotriphenylmethane.

(3) The **aurin group,** derived from trihydroxytriphenylmethane.

(4) The **phthaleins,** derived from phthalophenone.

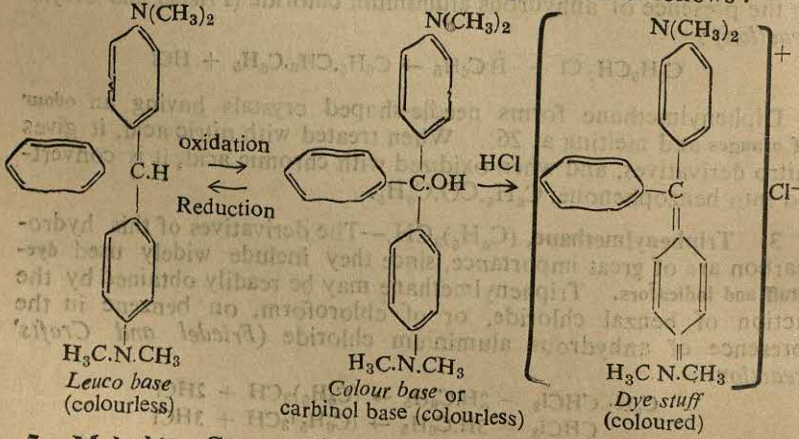
The formation of a triphenylmethane dye involves three distinct stages :—

(1) Formation of a **leuco base,** which is colourless, and can be obtained by the reduction of the dyestuff.

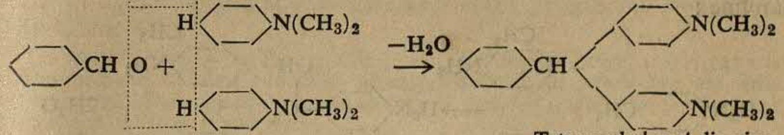
(2) Formation of a **colour base** (colourless), which is obtained by the oxidation of the leuco base. Being a derivative of triphenyl carbinol, it is also termed **carbinol base.**

(3) Formation of the **dyestuff** proper, which is a salt derived from the carbinol base and possesses a quinonoid structure.

The three stages in the case of malachite green are as follows :



5. Malachite Green.—The leuco base of this important green dye is prepared by heating benzaldehyde with dimethylaniline in the presence of zinc chloride :



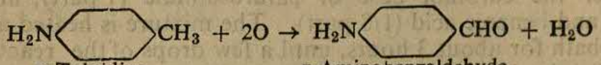
Tetramethyl-*p,p'*-diamino-triphenylmethane
(leuco base)

A well cooled solution of the leuco base in hydrochloric acid, when oxidized with lead dioxide, yields the carbinol base. The latter is then boiled with an acid (such as oxalic acid) to get the dye.

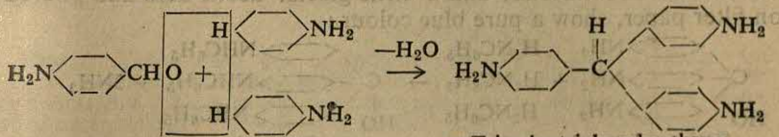
Malachite green (which is placed on the market usually as the oxalate) dyes wool, silk and leather directly and cotton mordanted with tannin.

6. **Rosaniline Group.**—The dyes of this group are derived from tri-*p*-aminotriphenylmethane.

Pararosaniline. This dye is manufactured by heating a mixture of *p*-toluidine (1 mole) and aniline (2 moles) with an oxidizing agent (arsenic acid or nitrobenzene). It is supposed that first the methyl group of *p*-toluidine gets oxidized to the aldehyde group, and the resulting *p*-aminobenzaldehyde condenses with aniline as in the malachite green synthesis. At the same time, the leuco base which may be supposed to be first formed, gets oxidized to the carbinol base :

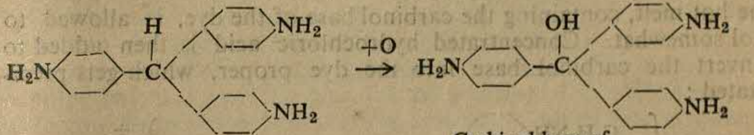


p-Toluidine *p*-Aminobenzaldehyde



Aniline
(2 molecules)

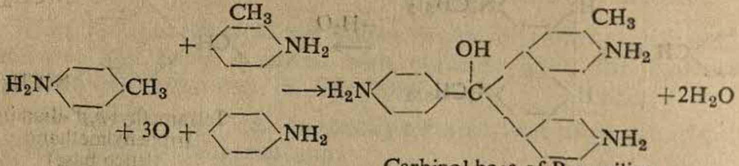
p-Triaminotriphenylmethane
(Paraleucaniline)



Carbinol base of
Pararosaniline

The colourless carbinol base, being triacid, combines with three molecules of hydrochloric acid with loss of water yielding pararosaniline chloride or **parafuchsine**. This forms crystals of a brilliant green colour, which show a metallic lustre and dissolve in water to give a purple-red solution. It dyes wool and silk directly and cotton when mordanted with tannin.

Rosaniline is a homologue of pararosaniline, and is obtained by oxidizing an equimolecular mixture of *p*-toluidine, *o*-toluidine, and aniline :

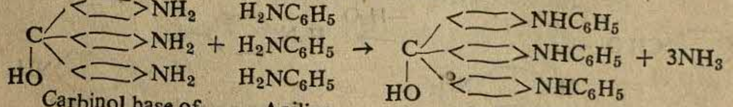


Carbinol base of Rosaniline

The carbinol base of rosaniline, like the corresponding derivative of pararosaniline, is a colourless tri-acid base. The salt containing one molecular proportion of hydrochloric acid is put on the market under the name of **fuchsine**, which resembles parafuchsine in forming green coloured crystals. It dissolves in water, giving a rose-red solution, and dyes silk and wool directly and cotton when mordanted with tannin and potassium hydrogen tartrate. The dye is not fast to light. With an excess of hydrochloric acid, rosaniline yields the acid salt, $C_{20}H_{20}N_3Cl.3HCl$, which gives a yellowish brown solution.

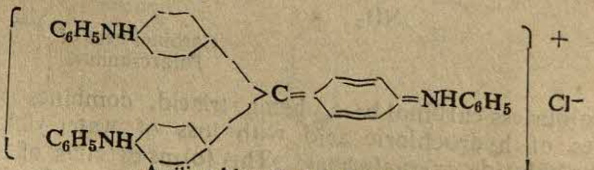
Expt. 1. Place a mixture of 2 gm. each of *p*-toluidine, *o*-toluidine and aniline together with 12 gm. of syrupy arsenic acid in a boiling tube. Heat the tube for about an hour at 180°—190° in a sulphuric acid bath. The product, which consists of *rosaniline arsenate*, will be found to dissolve in water to give a bright pink colour.

Aniline Blue (Triphenylrosaniline). This dye is prepared by heating together the carbinol base of pararosaniline (1 part), aniline (20 parts) and benzoic acid (1/8 part). The mixture is heated at 180° on a sandbath for about 3 hours, until a few drops of the reaction mixture, dissolved in alcohol and a little glacial acetic acid and poured on filter paper, show a pure blue colour :



Carbinol base of pararosaniline — Aniline (3 molecules) — Carbinol base of aniline blue

The hot melt, containing the carbinol base of the dye, is allowed to cool somewhat. Concentrated hydrochloric acid is then added to convert the carbinol base into the dye proper, which gets precipitated :



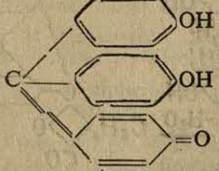
Aniline blue (hydrochloride)

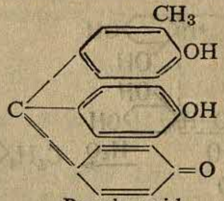
The dye is filtered hot at the pump, and washed with boiling water containing a few drops of concentrated hydrochloric acid. It is then dried on the water bath.

Aniline blue is a pure blue dyestuff. Like other rosaniline dyestuffs, it dyes wool and silk directly and cotton after being mordanted with tannic acid.

*7. **Aurin Group.**—The dyes of this group are derived from trihydroxy-triphenyl-methane. Unlike malachite green, rosaniline, etc., they are not salts but quinones. They are of little importance as dyes, but are chiefly employed as lakes in the wall-paper industry.

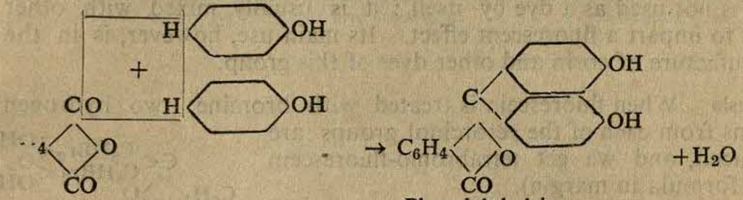
The two important members of this group are **aurin and resolic acid.**


Aurin


Rosolic acid

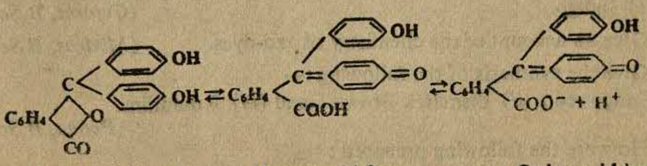
8. Phthaleins.—Phthaleins are derived from diphenylphthalide or *phthalophenone.* They are obtained by the condensation of phthalic anhydride with phenols.

Phenolphthalein, (*p,p-dihydroxy-diphenylphthalide*). The simplest member of this group, is prepared by heating phthalic anhydride and phenol to 120°, in the presence of concentrated sulphuric acid :


Phenolphthalein

Expt. 2. Take about 2 gm. of phthalic anhydride, 4 gm. of phenol, and 1 ml. of concentrated sulphuric acid in a test tube. Heat the mixture at 115°—120° for a short time. Allow to cool somewhat, and pour the product into a beaker full of water. Alkalify with sodium hydroxide; a pink colour is developed, which, on the addition of acid, gets discharged.

Phenolphthalein is a white, crystalline substance melting at 250°. It is readily soluble in alcohol but insoluble in water. It dissolves in alkali to give a strong red solution, from which it is reprecipitated in the colourless state by the addition of acid. This shows that phenolphthalein is a *pesudo-acid.* On the addition of alkali, the colourless lactone-form passes into the true acid-form, which has a quinonoid structure : the addition of acid produces the reverse change :

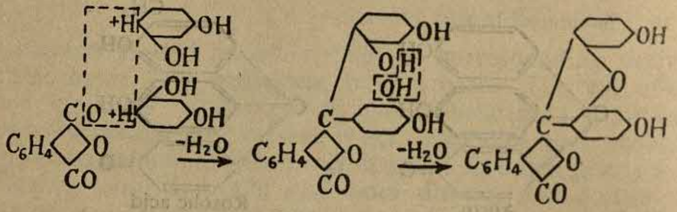

Lactone form
(colourless)

Quinonoid form
(coloured)

Quinonoid ion
(coloured)

On these facts is based the use of phenolphthalein as an indicator in acidimetry. It is, however, not used as a dye.

Fluorescein, (*Resorcinolphthalein anhydride*). This is obtained by heating recorsinol with phthalic anhydride at 200° (no condensing agent need be used). The tetrahydroxy intermediate compound, being unstable, loses a molecule of water, yielding fluorescein :

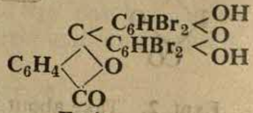


(unstable) Fluorescein

Fluorescein is a red, insoluble powder. It dissolves in alkali to give a yellowish red solution with a magnificent green fluorescence. This characteristic of fluorescein and other phthaleins of similar constitution is used as a *test* for phthalic anhydride and meta-dihydric phenols. Because of its faint colour, which soon fades away, fluorescein is not used as a dye by itself ; it is usually mixed with other dyes to impart a fluorescent effect. Its main use, however, is in the manufacture of eosin and other dyes of this group.

Eosin. When fluorescein is treated with bromine, two hydrogen atoms from each of the resorcinol groups are replaced, and we get tetrabromo-fluorescein (see formula in margin).

The potassium salt of the product is used as a dye under the name of *eosin*. This dyes wool and silk in fine shades of red, and is much used in the manufacture of red ink.



Eosin

QUESTIONS

1. Describe the preparation of phenolphthalein and discuss its structure. Explain its use as an indicator. (*Allahabad, M.Sc., Previous, 1930*)

2. How are *any three* of the following substances prepared ?
(*a*) Eosin, (*b*) Phenolphthalein, (*c*) Malachite-green, (*d*) Rosaniline. (*Punjab, B.Sc., 1939*)

3. Discuss the synthesis of the following :—(*a*) Methyl orange, (*b*) Malachite green, (*c*) Indigo. (*Gujarat, B.Sc., 1955*)

4. Give an account of the chemistry of azo-dyes. (*Madras, B Sc., 1955*)

5. Give the synthesis of the following :—
(*i*) Congo red ; (*ii*) Bismarck Brown ; and (*iii*) Rosaniline. (*Poona, B.Sc., 1955*)

6. How are the following prepared :
(*a*) malachite green, (*b*) fluorescein, (*c*) methyl orange. (*Andhra, B.Sc., 1957*)

7. While triphenylmethane is not a dye by itself, it is the parent substance of a very large number of important dye-stuffs. What important changes, when brought about into the composition and constitution of this hydrocarbon, succeed in producing tinctorial properties as required in a dye ?

What class of dyes are obtained from this parent hydrocarbon ?

Describe the preparation of the dyes belonging to this group.

(*Punjab*, *Honours School in Technical Chemistry*, *1929*)

8. "Triphenylmethane is the parent hydrocarbon from which various brilliant basic dyes are obtained". Give three instances in support of this statement, with equations, to show their derivation from the parent substance. How any one of these derivatives is prepared ? (*Punjab*, *B.Sc.*, *1924*)

9. Give the preparation and uses of : (*i*) Fluorescein, (*ii*) Congo Red, (*iii*) Malachite Green, (*iv*) Methyl Orange. (*Bombay*, *B.Sc.*, *1953*)

10. What are the triphenylmethane dyes ? How would you prepare malachite green and pararosaniline ? (*Punjab*, *B.Sc.*, *1946*)

11. Name three direct dyes for cotton and show how they are prepared. Give a brief note on the relation between colour and constitution.

(*Kerala*, *B.Sc.*, *1957*)

12. Give an account of the triphenylmethane dyes.

(*Jammu & Kashmir*, *B.Sc.*, *1958*)

13. How is phenolphthalein prepared ? Describe its important properties and uses. (*Punjab*, *B.Sc.*, *1959*)

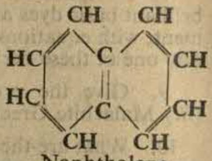
14. Give an account of triphenylmethane dyes. (*Patna*, *B.Sc.*, *1960*)

15. Mention the various types of dyes ; give examples. How is alizarin manufactured ? Discuss its synthesis and structure. (*Annamalai*, *B.Sc.*, *1962*)

CHAPTER FIFTY-TWO

NAPHTHALENE AND ITS DERIVATIVES

1. Naphthalene.—Naphthalene, $C_{10}H_8$, is an example of a *condensed ring compound.* Its molecule consists of two benzene nuclei linked together in such a way that a pair of carbon atoms is held in common between them, as shown in the margin.


Naphthalene

Naphthalene occurs in coal-tar in larger proportion than any other hydrocarbon. Its isolation from this source has already been described (page 543, sec. 5).

Crude naphthalene is purified by sublimation. Further purification is effected by dissolving it in petroleum ether in a steam-heated iron pan provided with a reflux condenser, allowing the solution to cool, and separating the crystals in a centrifugal machine and drying.

Properties. Naphthalene forms shining plates, having an unpleasant, penetrating odour. It melts at 79°, boils at 218°, and sublimes readily. Its volatility and great toxic power for the lower form of life render naphthalene useful as a preventive against moths. It is insoluble in water, but dissolves readily in ether or hot alcohol.

Naphthalene resembles benzene in chemical behaviour, and can be nitrated, sulphonated and halogenated in the same manner as benzene. The products, moreover, show similar reactions to the benzene derivatives. Thus the amino compounds can be diazotized and the sulphonic acids yield phenols (naphthols) on fusion with alkali.

Naphthalene forms addition products with hydrogen and chlorine. These are discussed in sections 5 and 12.

When submitted to oxidation with concentrated sulphuric acid in the presence of mercuric sulphate, naphthalene yields phthalic acid (chap. 50, sec. 7). The same product is also formed when the hydrocarbon is oxidized with air in the presence of vanadium pentoxide or potassium permanganate in acid solution. Oxidation with chromic acid, however, yields *alpha*-naphthaquinone. (sec. 10).

Naphthalene forms an additive compound with one molecule of picric acid. This is known as **naphthalene picrate**, and is formed when concentrated solutions of the two compounds in benzene are mixed. It crystallizes as yellow needles (*m.p.* 149°), and its formation is used for the identification[1] of the hydrocarbon.

---

[1] Many naphthalene derivatives (and also anthracene, phenanthrene and other compounds containing condensed nuclei) form analogous additive products with picric acid. These generally have sharp melting points and serve as useful derivatives in the identification of such substances.

Uses. Naphthalene is one of the most important of the industrial organic chemicals, and is put to the following uses :—

(1) Its use in the form of "moth balls" to protect woollens from damage by moths is well known.

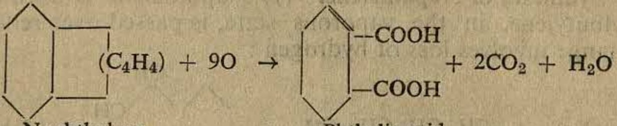
(2) Its oxidation to phthalic anhydride is extensively employed in the production of resins, lacquers, plastics and dyestuffs.

(3) Its derivatives find extensive application in the manufacture of explosives, photographic chemicals, soap, insecticides, disinfectants, synthetic tannins, etc.

2. Constitution of Naphthalene.—The constitution of naphthalene, $C_{10}H_8$, follows from the following considerations :—

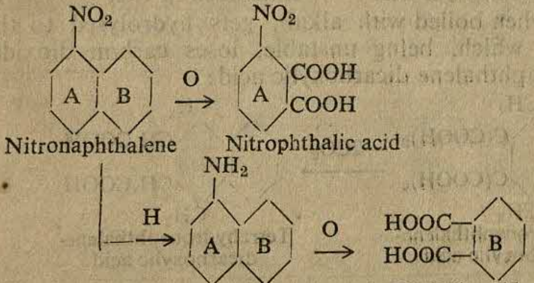
(1) It shows typical aromatic characteristics, and can be chlorinated, nitrated, and sulphonated, just like benzene. This indicates the presence of one or more aromatic nuclei in the molecule.

(2) When subjected to oxidation, it gives phthalic acid. This shows that the naphthalene molecule contains a benzene nucleus linked in the *ortho-position* to two separate side-chains or the two ends of a closed-chain. The reaction may be represented as follows :



Naphthalene Phthalic acid

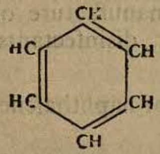
(3) α-Nitronaphthalene, obtained by the action of nitric acid on the hydrocarbon, yields, on oxidation, nitrophthalic acid. If, however, the nitronaphthalene be reduced to aminonaphthalene, and the latter compound submitted to oxidation, phthalic acid is produced, and *not* aminophthalic acid. These observations lead us to the conclusion that **naphthalene molecule contains two benzene nuclei having two carbon atoms in common.** In the oxidation of nitronaphthalene one of these rings (*i.e.*, the one marked *A*) is left intact, while the other one, *B*, is destroyed. The oxidation of aminonaphthalene, on the other hand, results in the destruction of the ring *A*, while *B* is preserved. These changes are shown below :



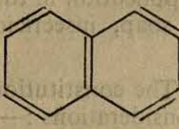
Aminonaphthalene Phthalic acid

The above formula for naphthalene, which was first suggested by Erlenmeyer in 1866, is fully confirmed by the various syntheses of naphthalene and its derivatives (sec. 3). It is also in entire agreement with the isomerism of naphthalene derivatives (sec. 4).

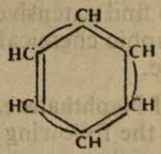
Naphthalene, however, differs from benzene in readily forming additive compounds, the **addition beginning at the α-positions.** This difference, though not obvious from Erlenmeyer's formula, is very well brought out by **Thiele's partial valency formula** :—



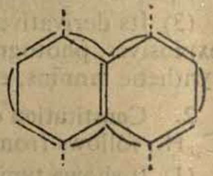
Benzene
(Kekule's formula)



Naphthalene
(Erlenmeyer's formula)



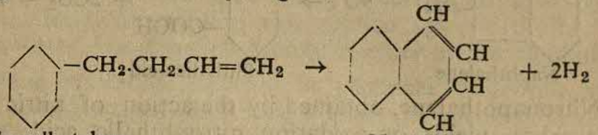
Benzene
(Thiele's formula)



Naphthalene
(Thiele's formula)

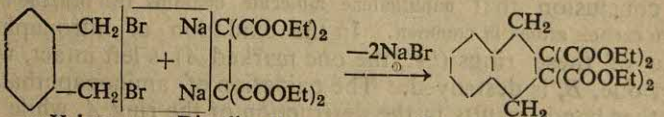
Whereas in the case of benzene there are no free partial valencies, the molecule of naphthalene has, according to Thiele's formula, **four free valencies available at the α-positions.**[1]

3. Syntheses of Naphthalene.—(1) Naphthalene is formed, when phenylbutylene, in the vaporous state, is passed over red-hot lime; the change involves loss of hydrogen :



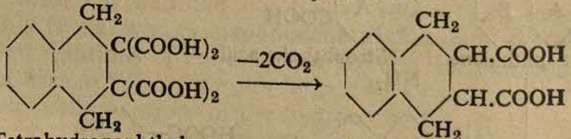
4-Phenylbutylene Naphthalene

(2) When *o*-xylene dibromide is treated with the disodio-derivative of ethane-tetracarboxylic ester, tetrahydronaphthalene-tetracarboxylic ester is produced :



o-Xylene dibromide · Disodio-ethane-tetracarboxylic ester Tetrahydronaphthalene tetracarboxylic ester

The resulting ester, when boiled with alkali, gets hydrolysed to the corresponding acid, which, being unstable, loses carbon dioxide, yielding tetrahydronaphthalene dicarboxylic acid :

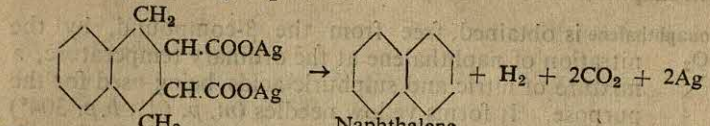


Tetrahydronaphthalene-tetracarboxylic acid Tetrahydronaphthalene-dicarboxylic acid

---

[1] Each of the two central partial valencies can only neutralize a *part* of the residual valencies at the two α-positions in its immediate neighbourhood. Hence there still remains a surplus of free partial valency at each of the four points as shown in the Thiele formula.

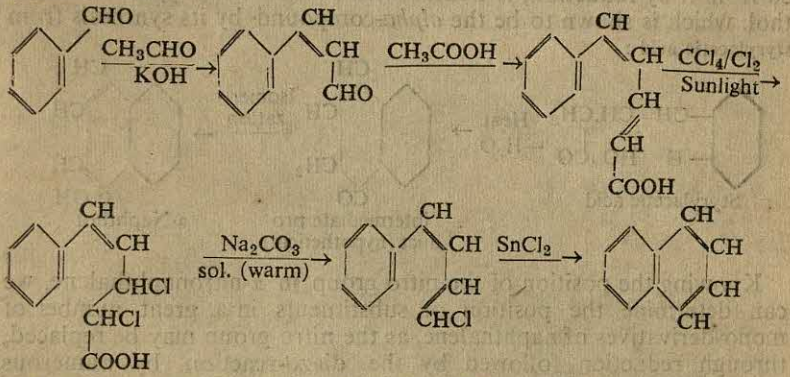
The silver salt of the dicarboxylic acid, when subjected to distillation, loses silver (2 atoms), hydrogen (2 atoms), and carbon dioxide (2 molecules), yielding naphthalene:



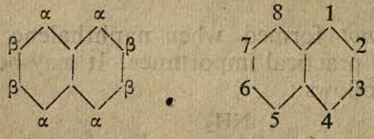
Silver tetrahydronaphthalene-dicarboxylate

Naphthalene

(3) Dr. S. A. Faseeh has developed a new synthesis (1953) of naphthalene. Starting with benzaldehyde, the various steps in the synthesis are :—



4. Isomerism of Naphthelene Derivatives.—The positions of substitutes in the naphthalene molecule are indicated according to either of the following systems :

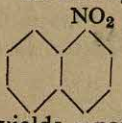


By reference to the above schemes, it can be seen that monoderivatives of naphthalene can exist in *two* forms (termed α- and β-, or 1- and 2-). The di-derivatives in which the two substituents are similar exist in *ten* isomeric forms: if the substituents be different, the number of possible isomers rises to *fourteen*. With the entry of three or more substituents into the molecule the number of isomerides becomes very much larger.

The disubstitution products of naphthalene in which the substituents occupy 1,8- or 4,5- positions (termed the *peri*-positions) are called peri-derivatives. Compounds containing two substituents in adjacent positions correspond in behaviour to the ortho-derivatives of benzene. They readily undergo anhydride formation and condensation. The peri-derivatives exhibit this behaviour in an enhanced degree.

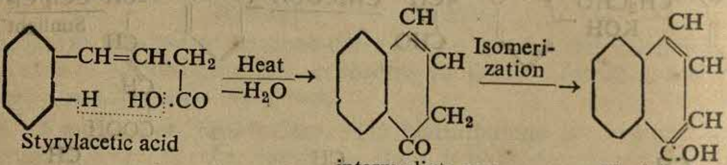
5. Halogen Derivatives of Naphthalene.—These are of little importance. When naphthalene is chlorinated at its boiling point, it yields **α-chloronaphthalene** (*b. p.* 263°). **β-Caloronaphthalene** (*m.p.* 61°), which is *not* formed by direct chlorination of the hydrocarbon, may be obtained from **β-naphthol** by the action of phosphorus pentachloride. The two **bromonaphthalenes** are prepared in the same manner as the corresponding chloro-derivatives. The halogen atom in these compounds, though not so firmly attached as in the corresponding benzene-derivatives, is not replaceable by boiling with alkalis.

6. Nitronaphthalenes.—



α-Nitronaphthalene is obtained, free from the β-compound, by the nitration of naphthalene at the ordinary temperature, a mixture of nitric and sulphuric acids being used for the purpose. It forms yellow needles (*m. p.* 61°; *b.p.* 304°) soluble in alcohol. When subjected to reduction, it yields α-naphthylamine, the reaction being of technical importance.

α-Nitronaphthalene is also of great importance in connection with the **orientation of naphthalene derivates.** With the naphthylamine, obtained from it by reduction, is treated with nitrous acid it yields a naphthol, which is shown to be the *alpha*-compound by its synthesis from **styrylacetic acid :**



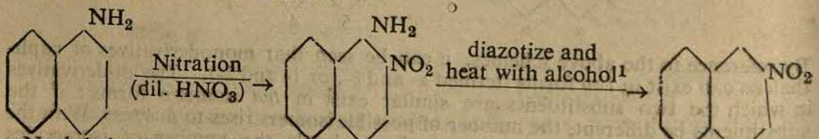
Styrylacetic acid

intermediate product (hypothetical)

α-Naphthol

Knowing the position of the nitro group in α-nitronaphthalene, we can determine the position of substituents in a great number of mono-derivatives of naphthalene, as the nitro-group may be replaced, through reduction followed by the diazo-reaction, by numerous atoms or groups. When a mono-derivative of naphthalene has been shown to be the α-compound, its isomeride must evidently be the β-compound.

β-nitronaphthalene is *not* formed when naphthalene is subjected to nitration and is of no practical importance. It may be obtained from α-naphthylamine as follows :



α-Naphthylamine

β-Nitro-α-naphthylamine

β-Nitronaphthalene

β-Nitronaphthalene forms yellow crystals melting at 79°.

7. Naphthalenesulphonic Acids.—When naphthalene is heated with concentrated sulphuric acid, at a temperature not exceeding 80°, **α-naphthalenesulphonic acid**, is obtained as the principal product. If the sulphonation of naphthalene be carried out at 160°, or if α-naphthalenesulphonic acid be heated with sulphuric acid at this temperature, **β-naphthalenesulphonic acid**, is obtained. Both the isomerides are deliquescent, crystalline acids. When fused with caustic alkalis, they yield the corresponding naphthols, the reaction being of commercial importance :

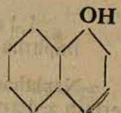
---

[1] The diazonium salt first produced is *reduced* by alcohol, the latter being oxidized to acetaldehyde.

$$C_{10}H_7SO_3Na + 2NaOH \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O$$

8. Naphthols.—

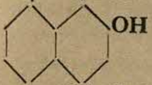
α-Naphthol is prepared on a large scale from naphthalene-α-sulphonic acid by fusion with alkalis.



Sodium naphthalenesulphonate is melted under pressure with 2 parts of caustic soda and a little water in an iron vessel provided with a stirring arrangement. The sodium naphtholate thus obtained is treated with dilute sulphuric acid, when naphthol is precipitated. It is separated and purified by distillation.

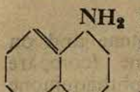
The synthesis of α-naphthol from styrlacetic acid already described (sec. 6, p. 690) proves the position of the hydroxyl group in the molecule.

α-Naphthol (*m. p.* 94°, *b. p.* 280°) crystallizes in needles possessing a faint, phenolic odour. It is only sparingly soluble in hot water but dissolves readily in alcohol and ether. The aqueous solution of α-naphthol gives with ferric chloride a violet, flocculent precipitate[1]. When heated with ammonia, α-naphthol yields α-naphthylamine, the hydroxyl group being replaced by $-NH_2$ group (contrast phenols). It can be sulphonated and nitrated in the usual manner to give products which are important dye intermediates.



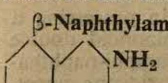
β Naphthol is prepared by fusing naphthalene-β-sulphonic acid with caustic potash. It melts at 122°, and boils at 286°. It is a colourless, crystalline substance having a faint phenolic odour, and differs from the α-compound in being readily soluble is hot water. With ferric chloride, it yields a green coloration and a flocculent precipitate of β-dinaphthol, $HO.C_{10}H_6.C_{10}H_6.OH$. When heated with ammonia, it yields β-naphthylamine.

9. Naphthylamines.—The amino derivatives of naphthalene and their sulphonic acids are much used in the manufacture of azo dyes.



α-Naphthylamine is prepared on a large scale by reducing α-nitronaphthalene with iron and hydrochloric acid. It is a solid having an unpleasant, faecal odour, and melts at 50°. Aqueous solutions of its salts give a blue precipitate with ferric chloride and other oxidizing agents (distinction from β-naphthylamine).

When α-naphthylamine is treated with fuming sulphuric acid, it yields 1-naphthylamine-4-sulphonic acid or **naphthionic acid**, which is used in the manufacture of Congo Red.



β-Naphthylamine is prepared on a large scale by heating β-naphthol with ammonia and zinc chloride in an autoclave. It differs from the α-compound in being odourless, and gives no coloration with oxidizing agents. It melts at 112°, and boils at 294°.

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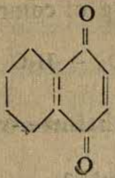
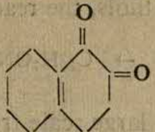
[1] This probably consists of iron compound of α-di-naphthol, $HO.C_{10}H_6C_{10}H_6OH$, an oxidation product of α-naphthol.

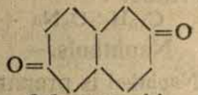
10. Naphthaquinones. Three quinones of naphthalene are known



1,4 of α-
naphthaquinone



1,2 or β-
naphthaquinone



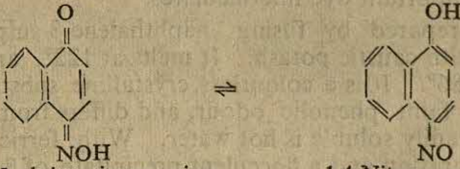
2,6- or amphi-
naphthaquinone

α-Naphthaquinone corresponds to *p*-benzoquinone, and is formed when certain α-derivatives or 1,4 diderivatives of naphthalene (*e.g.*, α-naphthylamine, 1,4-diaminonaphthalene, 1,4-aminonaphthol) are oxidized with chromic acid. It is usually prepared by oxidizing naphthalene with a boiling solution of chromic acid in glacial acetic acid (a method *not* applicable in the case of benzoquinone).

α-naphthaquinone is **similar in properties to *p*-benzoquinone.** It crystallizes from alcohol in deep-yellow needles (*m.p.* 125°), has a pungent smell, and is very volatile, subliming readily even at 100°.

It reacts with hydroxylamine to give a mono- and a dioxime. On reduction with sulphurous acid, it yields 1,4-dihydroxynaphthalene. When oxidized with nitric acid, it gives phthalic acid.

The monoxime of α-naphthaquinone is found to be identical with the compound formed by the action of nitrous acid on α-naphthol. Hence it may also be considered as 1,4-nitrosonaphthol :



α-Naphthaquinone oxime 1,4-Nitrosonaphthol

This offers another interesting case of *tautomerism*, which is analogous to that of *p*-nitrosophenol.

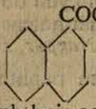
β-Naphthaquinone corresponds to *o*-benzoquinone, and is obtained by the oxidation of 1,2-aminonaphthol with chromic acid. It crystallizes in red needles, which decompose at 115° without melting. It is non-volatile, and therefore odourless (compare *o*-benzoquinone).

β-Naphthaquinone shows the **chemical behaviour of an orthodiketone** and on reduction with sulphurous acid, yields 1,2-dihydroxynaphthalene (compare *o*-benzoquinone, which gives catechol, 1,2-dihydroxybenzene). β-Naphthaquinone forms two monoximes, which are identical with 1,2-nitrosonaphthols (compare α-naphthaquinone monoxime).

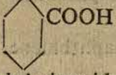
Amphi-naphthaquinone, or 2,6-naphthaquinone, is obtained by oxidizing the corresponding dihydroxynaphthalene, suspended in benzene, with lead dioxide. It forms odourless, non-volatile yellowish red prisms.

Amphi-naphthaquinone differs from the α- and β-compounds in possessing a true naphthaquinonoid structure ; in the other two. one of the quinonoid double bonds also forms a part of an aromatic nucleus. For this reason, amphi-naphthaquinone closely resembles *p*-benzoquinone in being an active oxidizing agent. Like the latter, it oxidizes instantaneously a cold, dilute solution of hydrogen iodide, turns ferrous ferrocyanide blue, and oxidizes sulphurous acid. β-Naphthaquinone is a milder oxidizing agent, and oxidizes ferrous ferrocyanide and sulphurous acid, though it has no effect on hydrogen iodide. α-Naphthaquinone oxidizes only sulphurous acid.

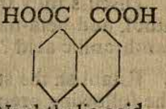
11. Naphthalenecarboxylic Acids.—These resemble the corresponding derivatives of benzene in formation and properties. The following three may be mentioned as examples :



α-Naphthoic acid



β-Naphthoic acid



Naphthalic acid

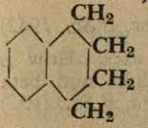
α-Naphthoic acid, or *naphthalene-α-carboxylic acid,* may be obtained by the action of carbon dioxide on α-naphthyl magnesium bromide. It melts at 160°, and, when heated further, loses carbon dioxide, yielding naphthalene.

β-Naphthoic acid, resembles the α-compound in formation and properties. It melts at 182°.

Naphthalic acid, or *naphthalene-1,8-dicarboxylic acid* resembles phthalic acid ; when heated strongly, it yields an anhydride analogous to phthalic anhydride.

12. Hydrogenated Naphthalenes.—Hydrogenation of naphthalene, which can be effected by Sabatier and Senderens reaction and by various reducing agents, yields products in which 2, 4, 6, 8 and 10 atoms of hydrogen have been added. Of these, *tetralin* and *decalin* are the most important.

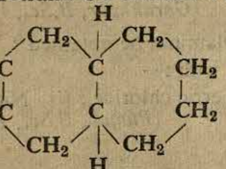
Tetralin *1,2,3,4-tetrahydronaphthalene,* is prepared on a large scale by the hydrogenation of naphthalene.



Naphthalene is first purified from sulphur and other compounds (which would poison the catalyst) by fusion with finely-divided metals of low melting point. The purified hydrocarbon is then treated with hydrogen (under a pressure of 10 to 15 atmospheres) in the presence of finely-divided nickel. The reaction which is an exothermic one, slows down when four atoms of hydrogen have been added.

Tetralin is a colourless liquid (*b.p.* 206° to 208° ; flash-point 72°). It is **used as a solvent in the preparation of varnishes and lacquers,** and in admixture with benzene and alcohol, as a motor fuel.

Decalin. $C_{10}H_{18}$, *decahydronaphthalene,* is prepared on a large scale by further hydrogenation of tetralin, using fresh catalyst[1]. Like tetralin it is **used as a solvent and a motor fuel.**



QUESTIONS

1. From what sources is naphthalene obtained? What products does it yield (*a*) on oxidation, (*b*) with H_2SO_4, (*c*) with HNO_3? (*London, B.Sc., 1931*)

2. An organic acid of the formula $C_{12}H_8O_4$ yielded a silver salt containing 50·2 per cent of silver. On heating the acid it is converted into a compound of the formula $C_{12}H_6O_5$, and on distillation with soda-lime, naphthalene is evolved. What is the acid? *Ans.* (Naphthalene-1,8-dicarboxylic acid)

3. How would you prepare a sample of pure naphthalene from coal tar. Establish its structure from its chemical properties and a synthesis. (*Lahore, B.Sc., 1954*)

4. How is naphthalene obtained? Starting with naphthalene how would you obtain (*a*) naphthol (*b*) naphthylamine, (*c*) anthranilic acid, (*d*) anthraquinone? (*Baroda, B.Sc., 1956*)

5. Describe one method of isolating a pure specimen of naphthalene from middle oil (a coal-tar product). Write equations to show the product or products

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[1] From the reaction mixture *two* stereoisomeric decalins can be separated by fractional distillation, *cis*-form, *b.p.* 193°, and *trans*-form, *b.p.* 185°.

formed when naphthalene is (*a*) hydrogenated ; (*b*) sulphonated ; and (*c*) chlorinated under different conditions separately. (*Rajasthan, B.Sc., 1958*)

6. Discuss fully the constitution of naphthalene. How will you obtain alpha-naphthol, and beta-naphthol from naphthalene ? How is naphthalene converted into anthranilic acid ? (*Nagpur, B.Sc., 1960*)

7. Establish the structure of naphthalene. Starting from naphthalene how are the following prepared ?

(*a*) β-Naphthol ; (*b*) β-Naphthylamine. (*Karnatak, B.Sc., 1961*)

8. What is the evidence on which the structure of naphthalene is based ? How are α-naphthylamine and β-naphthylamine obtained from naphthalene ? (*Andhra, B.Sc., 1961*)

9. Discuss the constitution of naphthalene. (*Lucknow, B.Sc., 1962*)

10. Discuss the constitution of naphthalene. Give a synthesis. How is naphthalene converted into (*i*) phenol and (*ii*) benzene ? (*Bombay, B.Sc., Chemistry, Subs., 1962*)

11. Discuss the structure of naphthalene. Comment on its aromatic character. How would you convert naphthalene into (*i*) Benzene and (*ii*) *alpha*-Naphthylamine. (*Bombay, B.Sc., Chemistry (Subs. . 1961*)

12. How has the constitution of naphthalene been established ? How will you obtain α-naphthol, β-naphthylamine and phthalic acid from it ? (*Saugar, B.Sc., 1962*)

13. How is naphthalene obtained ? Mention its properties and uses. How is its structure established ? How do you obtain from naphthalene alpha and beta naphthols ? (*Andhra, B.Sc., 1952*)

14. Starting from naphthalene, show, by means of equations how you would obtain :—

(*a*) β-naphthol ; (*b*) Anthranilic acid ; (*c*) β-nitronaphthalene ;
(*d*) Decalin ; (*e*) Naphthionic acid. (*Gorakhpur, B.Sc., 1962*)

15. How can alpha and beta naphthols and naphthylamines be obtained ? What products result when Beta-naphthol is reacted with :—

(*i*) Sodium and amyl alcohol ; (*ii*) Zinc dust ; (*iii*) Ferric chloride ; (*iv*) Nitrous acid. (*Punjab, B.Sc., 1962*)

CHAPTER FIFTY-THREE

ANTHRACENE AND ITS DERIVATIVES : PHENANTHRENE

1. Anthracene, $C_{14}H_{10}$.—Anthracene is a hydrocarbon of great commercial importance, since it is the starting material in the manufacture of alizarin and a number of other valuable dyestuffs. It is present in coal-tar to the extent of 0·25 to 0·45 per cent. During the coal-tar distillation, anthracene distils above 270° in what is called the "green oil" or "anthracene oil" fraction, which also contains phenanthrene, carbazole and some other compounds.

Isolation. Anthracene is obtained from the "*anthracene oil*" fraction of the coal-tar distillation, as described in sec. 7 on page 544.

Purification. To obtain pure anthracene, the commercial product is first distilled with one-third its weight of potassium carbonate to remove carbazole, $C_{12}H_8NH$, which forms the non-volatile potassium derivative, $C_{12}H_8NK$. The distillate, consisting almost entirely of anthracene and phenanthrene, is shaken with carbon disulphide, which dissolves out phenanthrene. The residue is crystallized from benzene, when pure anthracene is obtained.

Properties. Anthracene crystallizes from benzene in colourless lustrous plates, with a fine blue fluorescence. It melts at 216°, and boils at 351°. It is readily soluble in hot benzene, with difficulty in alcohol and ether, and is soluble in water. When saturated solutions of anthracene and picric acid in glacial acetic acid or benzene are mixed together, a precipitate of **anthracene picrate**, is formed. This consists of ruby-red needles (*m.p.* 130°). It differs from phenanthrene picrate in being resolved into its components by alcohol.

In **chemical behaviour**, anthracene resembles naphthalene more than any other hydrocarbon. Its more important reactions are—

(1) *Sulphonation.* When treated with sulphuric acid, anthracene yields a mono- and a di-sulphonic acid.

(2) *Action of Halogens.* With chlorine and bromine, it yields additive or substitution products, according to the conditions. Thus, when chlorine is passed into a cold solution of the hydrocarbon in carbon disulphide, we get *anthracene dichloride*, $C_{14}H_{10}Cl_2$. The interaction of chlorine and anthracene at 100° yields *9-10-dichloroanthracene*, $C_{14}H_8Cl_2$.

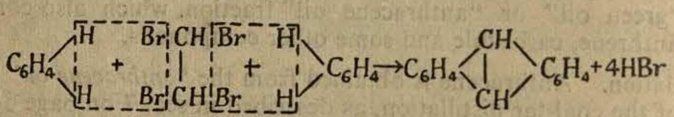
(3) *Oxidation.* Anthracene, like naphthalene, is oxidized by chromic acid, yielding *anthraquinone*, $C_{14}H_8O_2$. In fact, the oxidation

in this case takes place so readily, that nitric acid, under ordinary conditions, instead of effecting nitration[1] of anthracene, oxidizes it to anthraquinone.

(4) *Hydrogenation.* One of the outstanding properties of anthracene is its reduction to 9,10-*anthracene dihydride*, $C_{14}H_{12}$. This may be effected by sodium amalgam in alcoholic solution.

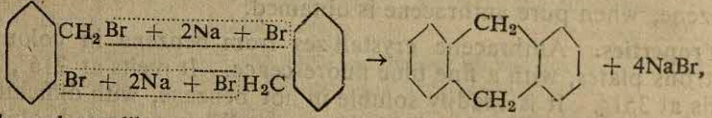
Further hydrogenation of the hydrocarbon yields the hydrides $C_{14}H_{16}$ and $C_{14}H_{24}$. It is interesting to note that the last named hydrocarbon is soluble in water.

2. Constitution of Anthracene.—The similarity of anthracene to naphthalene in chemical behaviour suggests a similarity in constitution. Anthracene has been synthesized in a number of ways. One of these, due to Anschutz, consists in heating benzene with acetylene tetrabromide in the presence of aluminium chloride :

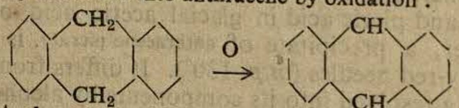


This synthesis shows that the anthracene molecule consists of two benzene nuclei linked through a $\begin{matrix}-CH-\\|\\-CH-\end{matrix}$ group, but it gives no information as to the actual point of union.

Now, when *ortho-bromobenzyl bromide* is heated with sodium, we get anthracene hydride,



which can be readily converted into anthracene by oxidation :



Anthracene hydride Anthracene

The above synthesis[2] proves that the two benzene nuclei are united to the group $\begin{matrix}-CH-\\|\\-CH-\end{matrix}$ through the *ortho*-carbon atoms of each nucleus. This is further supported by the synthesis of anthraquinone from phthalic anhydride and benzene (sec. 4, p. 697).

There has been much discussion about the disposition of the fourth valency unit of the two connecting carbons. According to Graebe and Liebermann, there exists a para linkage[3] across the central ring (formula 1), while Hinsberg supports the ortho-quinoniod formula (II). However, for practical purposes the formula is written without double bonds as at III :

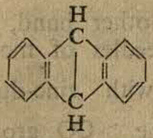
---

[1] When nitric acid acts on anthracene dissolved in glacial acetic acid containing acetic anhydride, nitration does occur, *9-nitro-anthracene* being formed.

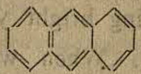
[2] In this synthesis of anthracene the isomeric hydrocarbon, *phenanthrene*, is formed at the same time, the reaction taking a different course.

[3] A grave objection against this view point is the great strain which would make the molecule highly unstable.

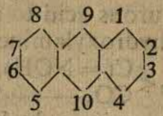
(I)



(II)



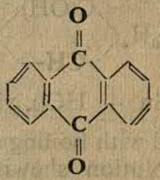
(III)



The position 1, 4, 5 and 8 are equivalent, and are termed *alpha* positions; 2, 3, 6 and 7 are termed *beta*, while 9 and 10 are called *gamma* or *meso*.

3. Isomerism of Anthracene Derivatives.—Monosubstitution products of anthracene exist in *three* different forms, α-, β-, and γ-. When two atoms of hydrogen are displaced by similar atoms or groups, as many as *fifteen* isomers may be obtained. A very large number of anthracene derivatives is known, though it is small as compared with the enormous number theoretically possible.

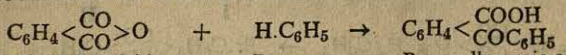
4. Anthraquinone, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, (also see formula in the margin), is one of the most important derivatives of anthracene, and is formed, as already mentioned, when the hydrocarbon is oxidized by chromic acid or nitric acid.



Preparation. (1) Anthraquinone is prepared on a large scale, for use in the manufacture of alizarin and other dyestuffs, by oxidizing crude anthracene, suspended in water, with sodium dichromate and sulphuric acid. The product is purified by heating with concentrated sulphuric acid at 100°. The impurities are converted into water-soluble sulphonic acids, while the anthraquinone dissolves unchanged. The acid solution is diluted with water, when anthraquinone is precipitated.

The precipitate is filtered, washed and purified by sublimation.

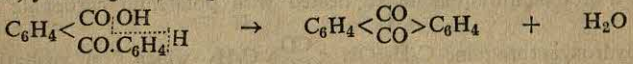
(2) Anthraquinone is also prepared on a large scale synthetically by treating a solution of phthalic anhydride in benzene with anhydrous aluminium chloride. The reaction occurs in two stages; *o*-benzoylbenzoic acid is first formed :



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O \quad + \quad H.C_6H_5 \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{COOH}{COC_6H_5}$$

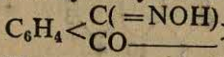
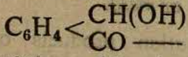
phthalic anhydride   Benzene   *o*-Benzoylbenzoic acid

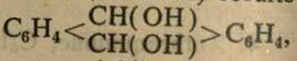
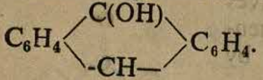
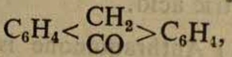
This, by the further action of aluminium chloride, loses a molecule of water, yielding anthraquinone :



$$C_6H_4<\genfrac{}{}{0pt}{}{CO.OH}{CO.C_6H_4.H} \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 \quad + \quad H_2O$$

Properties. Anthraquinone crystallizes from glacial acetic acid in pale-yellow needles melting at 285°. At a higher temperature, it sublimes readily, forming long sulphur-yellow prisms.

Anthraquinone is a very stable substance, and is attacked only with difficulty by oxidizing agents, nitric acid or sulphuric acid. In chemical behaviour, anthraquinone resembles aromatic ketones more closely than it does the para-quinones. It possesses no pungent smell, is not readily volatile, and is not reduced by sulphurous acid to a hydroquinone. On the other hand, it reacts with hydroxylamine, yielding bright yellow needles of monoxime,  $C_6H_4<{C(=NOH) \atop CO}>C_6H_4$. When warmed with zinc-dust and dilute sodium hydroxide solution, one of the >CO groups gets reduced to a >CHOH group with the production of **oxanthranol**,  $C_6H_4<{CH(OH) \atop CO}>C_6H_4$, which dissolves in the excess of alkali, giving a blood-red colour. The reaction is utilized as a test for anthraquinone.

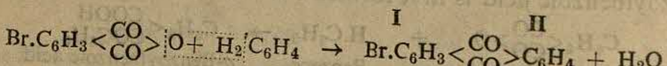
Further reduction in alkaline solution (Zn + NaOH) results in the formation of *anthrahydro-quinone*,  $C_6H_4<{CH(OH) \atop CH(OH)}>C_6H_4$, which being unstable loses a molecule of water, yielding **anthranol**,  $C_6H_4<{C(OH) \atop CH}>C_6H_4$. Reduction of anthraquinone in acid medium (Sn + HCl), yields **anthrone**,  $C_6H_4<{CH_2 \atop CO}>C_6H_4$, which, when treated with boiling alkali, is transformed into the tautomeric **anthranol**, the solution showing a bright blue fluorescence. On acidifying the solution, anthrone is regenerated. Anthrone is therefore a *pseudo*-acid, anthranol being the *aci*-form.

Finally, by distilling anthraquinone with zinc-dust in a current of hydrogen, anthracene itself is obtained.

Anthraquinone can be brominated, sulphonated and nitrated.

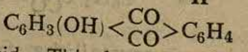
Constitution. The constitution of anthraquinone follows from its synthesis from phthalic anhydride and benzene through *o*-benzoic acid. Since the CO groups in phthalic anhydride occupy the *ortho*-position, it is clear that they must also do so in one of the benzene rings in anthraquinone. That they occupy the *o*-position in the second ring as well has been proved as follows :—

Bromophthalic anhydride condenses with benzene in the presence of aluminium chloride, yielding *bromanthraquinone* :



$$Br.C_6H_3<{CO \atop CO}>O + H_2C_6H_4 \rightarrow \overset{I}{Br.C_6H_3}<{CO \atop CO}>\overset{II}{C_6H_4} + H_2O$$

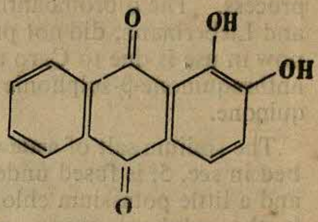
The formation of bromanthraquinone from bromophthalic anhydride proves, as before, that the two >CO groups are linked in the ring I in the *o*-position.

Now if bromoanthraquinone be heated with potassium carbonate at 160°, we get hydroxyanthraquine  $\underset{I}{C_6H_3(OH)}<{CO \atop CO}>\underset{II}{C_6H_4}$ which on oxidation with nitric acid yields phthalic acid. This shows that the two groups are linked to ring II also in the *o*-position, ring I having been destroyed during oxidation.

5. **Anthraquinone-β-sulphonic Acid.**—The sodium salt of this acid is used in considerable quantities in the manufacture of alizarin. The acid is prepared by heating anthraquinone at 160° with an equal weight of fuming sulphuric acid (containing 50 per cent SO_3) in enamelled iron vessels, provided with stirrers. The product is poured into water, when unchanged anthraquinone separates out. This is filtered off, and the solution is neutralized with sodium carbonate, the sparingly soluble sodium salt of anthraquinone-β-sulphonic acid separates from the cold solution in shining plates, and is collected in filter presses. The more

soluble sodium salts of anthraquinonedisulphonic acids (formed during sulphonation) are left behind in the solution.

6. **Alizarin,** 1, 2-*Dihydroxyanthraquinone.*—This most important derivative of anthraquinone has a splendid red colour, and ranks with indigo as the most valuable of dye-stuffs. Before the year 1869, it was exclusively obtained from madder (*Rubia tinctorum*), a shrub about three feet high, which was cultivated more especially in France. The root of this plant contains the glucoside **ruberythric acid,** $C_{26}H_{28}O_{14}$, with small quantities of other glucosides. When the madder extract is allowed to ferment, or boiled with a dilute mineral acid, the ruberythric acid that it contains is hydrolysed into alizarin (one molecule) and glucose (two molecules):



$$\underset{\text{Ruberythric acid}}{C_{26}H_{28}O_{14}} + 2H_2O \rightarrow \underset{\text{Alizarin}}{C_{14}H_8O_4} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Constitution. A dye of such great importance as alizarin naturally attracted the attention of organic chemists, who sought to prepare it artificially. The various points in proving the constitution of alizarin are—

(1) In 1865 Græbe and Liebermann heated it with zinc dust when anthracene sublimed out. This furnished the key to the constitution of alizarin. By comparing the formulae,

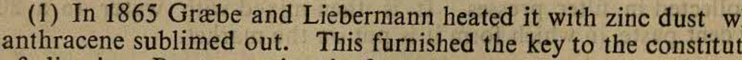
$$\underset{\text{Anthracene}}{C_{14}H_{10}} \qquad \underset{\text{Anthraquinone}}{C_{14}H_8O_2} \qquad \underset{\text{Alizarin}}{C_{14}H_8O_4}$$

it was assumed that alizarin was a *dihydroxyanthraquinone*.

(2) To test this hypothesis, Græbe and Liebermann fused dibromoanthraquinone[1] with potassium hydroxide, when fortunately alizarin was obtained.

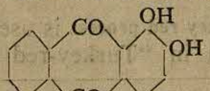
(3) The formation of phthalic acid by the oxidation of alizarin proved that both the hydroxyl groups are present in the *same* benzene ring.

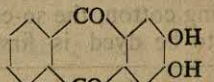
(4) Further, it was found that alizarin can be synthesised by heating phthalic anhydride at 150° with catechol (1,2-dihydroxybenzene) and sulphuric acid:



$$\underset{\text{Phthalic anhydride}}{C_6H_4{<}\substack{CO\\CO}{>}O} + \underset{\text{Catechol}}{C_6H_4{<}\substack{OH(1)\\OH(2)}} \rightarrow \underset{\text{Alizarin}}{C_6H_4{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{OH\\OH}} + H_2O$$

This shows that two hydroxyl groups in alizarin are *adjacent* to each other. Hence, the structural formula of alizarin may be either

(I) 

or (II) 

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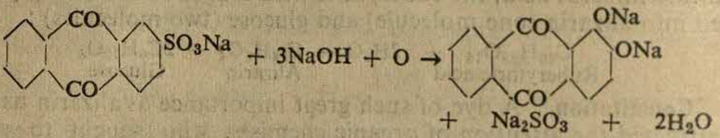
[1] Obtained by heating anthraquinone with bromine in the presence of a little iodine at 160° in a sealed tube.

(5) Now, there exist *two* isomeric nitro-alizarins, both having the nitro group in the same benzene ring as the hydroxyl groups. Hence, formula I, and not II, represents alizarin.

Manufacture. Alizarin is now prepared exclusively by a synthetic process. The dibromoanthraquinone method, discovered by Græbe and Liebermann, did not prove a commercial success. The method now in use is due to Caro and Perkin, who substituted the cheaper anthraquinone-β-sulphonic acid for the more expensive dibromaonthraquinone.

The sodium salt of **anthraquinone-β-sulphonic acid**, prepared as described in sec. 5, is fused under pressure at 180° with sodium hydroxide and a little potassium chlorate. Under these conditions, not only is the sulphonic group replaced by a hydroxyl group, but also a second hydroxyl group is formed by direct oxidation :



The fused mass is dissolved in water, and alizarin precipitated by the addition of sulphuric acid. The yellowish crystalline precipitate is collected in filter presses. It is then mixed with water to a 20 per cent paste, in which form it is put on the market.

Properties. From the commercial 20 per cent paste, pure alizarin can be obtained by recrystallization from toluene, or by sublimation. It forms beautiful, dark red prisms or needles melting at 290°. It is readily soluble in toluene, alcohol and ether but is only sparingly soluble in water, even when heated.

On account of its phenolic character, alizarin dissolves in aqueous alkalis, yielding deep purple solutions. Distillation with zinc-dust converts it into anthracene, a fact that gave the first insight into the constitution of alizarin.

Use. The value of alizarin as a dye-stuff depends on its power of yielding, with certain metallic oxides, insoluble, beautifully coloured compounds called "lakes". When a cotton or wool fabric is mordanted with one of these oxides, it can be dyed a brilliant, fast colour with alizarin, the actual colour obtained depending on the oxides used. With the oxides of aluminium and tin, the colour is bright red (Turkey-red), with chromium oxide brownish violet, with ferric oxide violet black, and with lime blue.

In dyeing cotton, the so-called **Turkey red process** is used. The cloth or yarn to be dyed is first steeped in "Turkey-red oil"[1]. After drying, it is mordanted by soaking in a solution of aluminium acetate. It is once again dried, and then placed in an alizarin bath containing Turkey-red oil and some chalk. The material is then steamed under pressure, and finally the colour is cleared by washing with soap.

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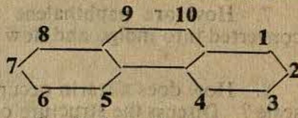
[1] Cold concentrated sulphuric acid is added gradually, with frequent stirring, into well-cooled castor oil. The product is washed with a solution of common salt, and then neutralized with ammonia. The resulting water-soluble liquid is put on the market under the name of *Turkey-red oil.*

7. **Phenanthrene**, $C_{14}H_{10}$.—This hydrocarbon is isomeric with anthracene, and is assigned the structure given in the margin. For naming the isomeric derivatives, the carbon atoms are numbered as shown.

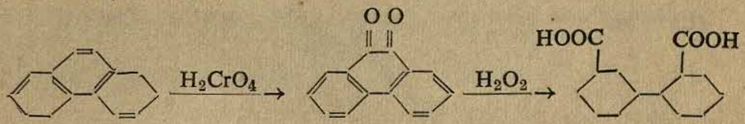


Phenanthrene occurs along with anthracene in "anthracene oil" of coal-tar distillation, and may be obtained from that source. The isolation of the hydrocarbon, however, is of little interest as all attempts to utilize it in the manufacture of dyes have had no success so far.

Physical Properties. Phenanthrene forms colourless, lustrous plates (*m.p.* 99°; *b.p.* 330°). It is readily soluble in benzene, ether, and alcohol, yielding solutions with blue fluorescence.

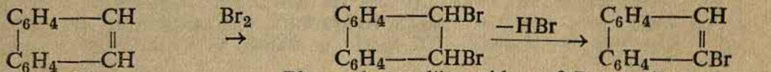
Chemical Properties. Phenanthrene forms a yellow picrate (*m p.* 145°).

The most reactive part of the phenanthrene molecule is the central, 9, 10-positions. Thus, oxidation with chromic acid ($K_2Cr_2O_7+96$ per cent H_2SO_4) yields the **9,10-phenanthraquinone**, which is an ortho-quinone with an orange colour and melting at 206°. It is readily purified by extraction with aqueous sodium bisulphite and decomposing the resulting water-soluble bisulphite compound with sodium hydroxide. Further oxidation with hydrogen peroxide in acetic acid solution causes a rupture of the quinone ring with the production of **diphenic acid** (diphenyl-o, o′-dicarboxylic acid).



Phenanthrene Phenanthraquinone Diphenic acid

Phenanthrene absorbs bromine readily, giving the 9,10-dibromide, which on being warmed, loses a molecule of hydrogen bromide and is converted into 9-bromophenanthrene :



$$\begin{array}{l}C_6H_4—CH\\ \,|\qquad\quad \|\\ C_6H_4—CH\end{array} \xrightarrow{Br_2} \begin{array}{l}C_6H_4—CHBr\\ \,|\qquad\quad |\\ C_6H_4—CHBr\end{array} \xrightarrow{-HBr} \begin{array}{l}C_6H_4—CH\\ \,|\qquad\quad \|\\ C_6H_4—CBr\end{array}$$

Phenanthrene Phenanthrene dibromide 9-Bromophenanthrene

Nitration of phenanthrene results in the production of a *mixture* of derivatives in which positions 2, 3, 4 and 9 are substituted by nitro groups. Separation of isomers is most difficult and the reaction, therefore, is of no practical value.

QUESTIONS

1. How is anthracene obtained on a commercial scale ? Discuss its structure. How is alizarin prepared from it ? (*Madras, B.Sc., 1944*)

2. Describe the preparation of anthraquinone and point out its importance in industry. (*Punjab, B.Sc., 1960*)

3. How does Alizarin occur in nature ? Show how its constitution is arrived at. Give its preparation on a large scale. Describe its use as a dye-stuff. (*Gujarat, B.Sc., 1956 ; Baroda, B.Sc., 1955*)

4. Discuss the constitution of anthracene. Compare its aromatic character with that of benzene. How is anthracene converted into alizarin ?
(*Poona, B.Sc., 1959*)

5. How is alizarin manufactured ? Describe its properties and structure.
(*Lahore, B.Sc., 1956*)

6. Establish the structure of alizarin. Give an account of its manufacture.
(*Mysore, B.Sc., 1957*)

7. How are naphthalene and anthracene obtained ? How is naphthalene converted into indigo and how is anthracene converted into alizarin ?
(*Andhra, B.Sc., 1961*)

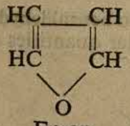
8. How does alizarin occur in nature and how can it be prepared on a large scale ? Discuss the structure of alizarin and give its use as a dye-stuff.
(*Gujarat, B.Sc., 1962*)

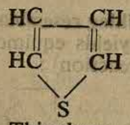
CHAPTER FIFTY-FOUR

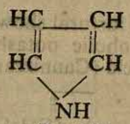
UNINUCLEAR HETEROCYLIC COMPOUNDS

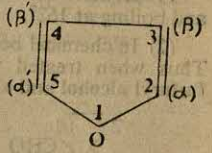
1. FURAN, THIOPHENE AND PYRROLE

1. The three most important five-membered heterocyclic rings are those present in *furan, thiophene and pyrrole* :


Furan

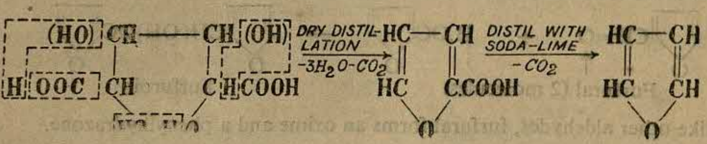

Thiophene


Pyrrole



For nomenclature purposes, the various positions of substituents in these rings are numbered, or lettered, as shown above for furan.

2. Furan, C_4H_4O.—This compound is of little importance. It occurs in the distillate of pine-wood tar, and may be obtained synthetically from *mucic acid* (the dibasic acid obtained by the oxidation of *d*-galactose).



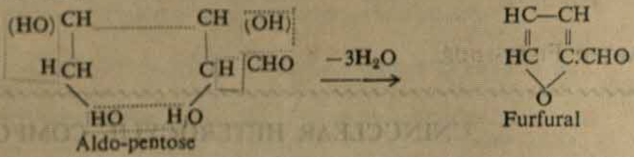
Mucic acid α-Furoic acid Furane

Preparation. The most practicable method of preparing furan involves dehydration of natural pentoses to furfural (sec. 3). The latter when treated with 33 per cent NaOH solution gives furfuryl alcohol and α-furoic acid (Cannizaro's reaction). α-furoic acid is heated at about 200°, when it loses carbon dioxide, and forms furan.

Properties. Furan is a colourless liquid, having a chloroform-like odour and boiling at 32°. It is soluble in water. Its vapour imparts a *green* coloration to a pine splint moistened with hydrochloric acid.

Constitution. The constitution of furan follows from its synthesis from mucic acid. The failure of the compound to react with metallic sodium and with hydroxylamine or phenylhydrazine is in agreement with the above view, and proves the absence of the hydroxyl or the keto group in the molecule.

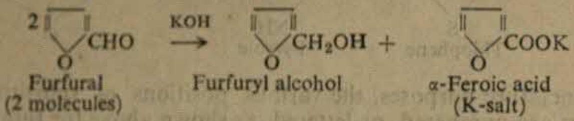
3. Furfural, or *Furfuraldehyde.*—This is the most important derivative of furan, and has been known for a long time. It is formed when bran, wood and various carbohydrates are distilled with sulphuric acid. The best method of its preparation consists in boiling arabinose, xylose, or *pentosans* with concentrated hydrochloric acid :



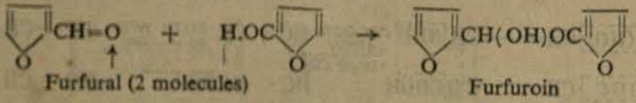
Manufacture. Furfural is manufactured on a large scale from corn-cobs, oat-hulls, cottonseed-hulls and rice-hulls. The Quaker Oats Company (a large cereal manufacturer in U.S.A.) is producing it from oat-hulls, obtained as a by-product in the manufacture of the well-known "Quaker Oats".

Properties. (1) Furfural is a colourless, oily liquid, having an agreeable odour and boiling at 162°.

(2) In chemical behaviour, furfural shows **striking resemblance to benzaldehyde.** Thus when treated with alcoholic potash it yields equimolecular quantities of **furfuryl alcohol** and **α-feroic acid** (Cannizzaro's reaction) :



With ammonia, it yields *hydrofurfuramide*, $(C_5H_4O)_3N_2$, analogous to hydrobenzamide (page 656). Further it gives Perkin's reaction and undergoes Claisen's condensation, and forms a green dye with dimethylamine (compare benzaldehyde). In presence of alcoholic potassium cyanide, it undergoes condensation, yielding **furfuroin** (compare "benzoin condensation").



Like other aldehydes, furfural forms an oxime and a phenylhydrazone.

(4) Furfural, like formaldehyde, undergoes condensation with phenols in the presence of suitable catalysts, yielding brownish black, resinous substances which resemble "Bakelite".

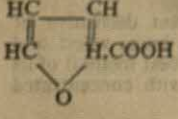
Tests. (1) When heated with aniline and hydrochloric acid, furfural yields an intensely red dye.

(2) It imparts a green colour to a pine-shaving moistened with hydrochloric acid.

Uses. (1) The largest commercial application of furfural is in the manufacture of a furfural-phenol molding resin, called "Durite" (p. 641).

(2) It is also employed in the manufacture of nylon, paints, automobile tyres, dye-stuffs and insecticides.

(3) Furfural is a valuable solvent for the purification of anthracene and for other purposes.



4. Pyromucic Acid, *α-Furoic Acid, Furane-α-carboxylic Acid.* This compound is obtained by the dry distillation of mucic acid (see sec. 2), and also by oxidizing furfural with silver oxide.

In physical properties, pyromucic acid resembles benzoic acid, and crystallizes in colourless leaflets, which sublimes readily at 100°. It melts at 134°, and, is readily soluble in hot water or alcohol.

In chemical behaviour, pyromucic acid resembles the aromatic compounds in but a few reactions. Thus when treated with fuming sulphuric acid it yields a sulphonic acid. In most of its reactions, however, it resembles unsaturated acids of the aliphatic series. Thus it instantaneously decolorizes an alkaline solution of potassium permanganate, and, when treated with bromine vapour, takes up four atoms of the halogen. When warmed with bromine water, it is converted into furmaric acid.

When heated at its boiling point, 200°, pyromucic acid undergoes decomposition into furan and carbon dioxide.

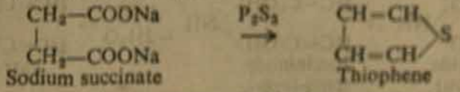
5. Thiophene, C_4H_4S (for structural formula, see sec. 1).—This compound occurs to the extent of about 0·5 per cent in the crude benzene obtained from coal-tar. Similarly, its homologues α-and β-methylthiophenes, or **thiotolenes,** $C_4H_3(CH_3)S$, and the dimethylthiophenes, or **thioxens,** $C_4H_2(CH_3)_2S$, occur in commercial toluene and xylene respectively[1]. Thiophene and its homologues may be isolated from commercial benzene, toluene and xylene by making use of the fact that they are more readily sulphonated than the benzene hydrocarbons.

Isolation.—

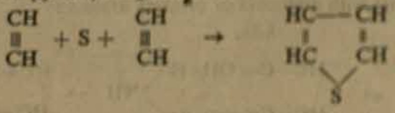
(1) **Victor Meyer's Method.** Thiophene may be isolated from crude benzene by repeated extraction with cold, concentrated sulphuric acid, until the residual benzene ceases to give the *indophenine reaction* (see under benzene). The sulphonic acid thus obtained is decomposed by superheated steam, when thiophene is regenerated.

(2) **Dimroth's Method.** A better and quantitative method, discovered by O. Dimroth in 1899, is based on the fact that thiophene is very much more readily mercurated than benzene (see under benzene). It consists in boiling crude benzene with mercuric oxide and acetic acid, when thiophene is precipitated as *thiophene-α, α-dimercuri-hydroxy acetate*, $CH_3COOHg.C_4H_2S.HgOH$. This compound is then distilled with moderately concentrated hydrochloric acid, whereby it gets decomposed into thiophene and mercuric chloride,

Synthesis. (1) Thiophene is best prepared synthetically by distilling sodium succinate with phosphorus trisulphide :—



(2) Another interesting synthesis of thiophene consists in the interaction of acetylene and iron pyrites, FeS_2, at about 300° :



Properties. (1) Thiophene is a colourless liquid having almost the same odour and boiling point (84°) as benzene (80°).

(2) In chemical behaviour, too, **thiophene closely resembles benzene,** being, as a rule, more reactive towards various reagents. Thus, as already mentioned, it is readily sulphonated by cold, concentrated sulphuric acid, and undergoes mercuration far more readily than benzene. Bromine reacts energetically with thiophene, forming chiefly *2,5-dibromo thiophene*, $C_4H_2Br_2S$. When thiophene is treated with a mixture of concentrated nitric acid and acetic anhydride, *mononitrothiophene* is produced. This is a solid (*m.p.* 44°) having an odour like that of nitrobenzene. When subjected to reduction, the nitro-compound yields *aminothiophene,* an

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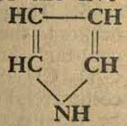
[1] Thiophene and its homologues possess practically the same boiling points as the corresponding benzene hydrocarbons : This explains their presence in commercial benzene, toluene and xylene.

unstable substance which changes quickly to a varnish-like mass. Aminothiophene cannot be diazotized, but it reacts with benzenediazonium chloride, yielding an orange coloured dyestuff.

Test. Thiophene is readily identified by the *indophenine reaction* given under Benzene.

α-Thiophenecarboxylic acid is obtained by the oxidation of α-methylthiophene. It resembles benzoic acid and crystallizes from hot water in needles (*m.p.* 12·5°).

6. Pyrrole, C_4N_4NH.—This is the most important of the five-membered heterocyclic compounds, several natural products containing the pyrrole ring being known, *e.g.*, nicotine, atropine, hyoscyamine, cocaine, the haemoglobin and chlorophyll.

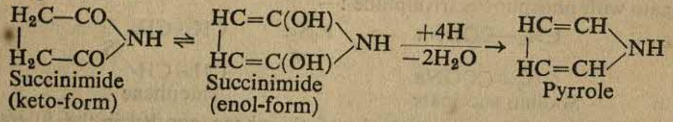


Occurrence. Pyrrole occurs in coal-tar and in Dippel's bone oil.

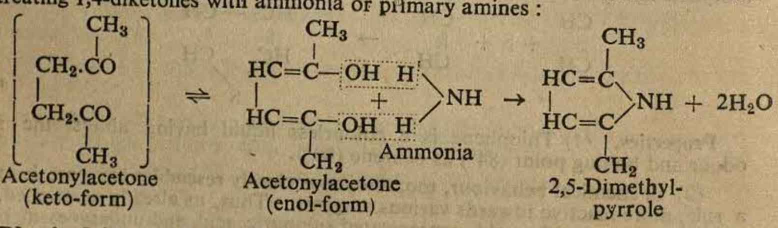
Isolation. Pyrrole is best prepared **from bone oil.** The oil is first fractionated, and the fraction passing between 120° and 130° is collected separately. This is freed from strongly basic substances, such as pyridine, by shaking with dilute sulphuric acid, dried and again fractionated. The liquid is then treated with metallic potassium, when the solid **potassium pyrrole,** C_4H_4NK, is formed. This is washed with ether, and decomposed with water, when pyrrole is regenerated.

Synthesis. Pyrrole and its derivatives have been synthesized by several methods, which prove the constitution of the pyrrole ring. The following two are illustrative examples :—

(1) When succinimide is reduced by means of zinc-dust and acetic acid, pyrrole is produced :



(2) A general method for the preparation of homologues of pyrrole consists in treating 1,4-diketones with ammonia or primary amines :



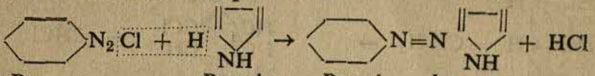
Physical Properties. Pyrrole is a colourless liquid, having an odour somewhat like that of chloroform. It boils at 131°, and turns brown on exposure to light. It is sparingly soluble in water, but dissolves readily in alcohol and ether.

Chemical Properties. Pyrrole possesses an aromatic character, and **resembles phenols** in many respects; *e.g.*,—

(1) Like phenols, it readily forms halogen substitution products,

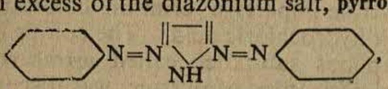
all the four methine hydrogen atoms being replaceable. The most important of the halogen derivatives of pyrrole is tetra-iodopyrrole or **iodole**, C_4I_4NH. It is produced by the action of iodine and alkali on pyrrole, and is used as **odourless substitute for iodoform.**

(2) Like phenols, pyrrole readily undergoes coupling with diazonium salts, yielding azo-compounds ; the linking occurs in the α- in preference to the β-position. Thus with benzene diazonium chloride, **pyrrole-azobenzene** is produced :*



Benzene-diazonium chloride Pyrrole Pyrrole-azobenzene

With an excess of the diazonium salt, **pyrrole-bisazobenzene**,

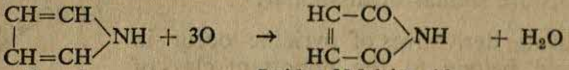


is formed

(3) Because of the >NH group being linked with the two strongly negative $-CH=CH-$ groups, pyrrole acts only as a **feeble base**. It dissolves slowly in dilute acids. With concentrated acids, it gets quickly resinified, so that it is not possible to convert it into the nitro and the sulphonic acid derivatives.

The strongly negative character of the $-CH=CH-$ groups confers, in fact, **acidic properties on the** >NH **group** in consequence of which pyrrole forms a potassium derivative, C_4H_4NK.

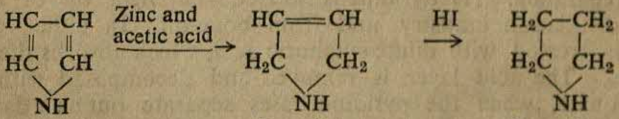
(4) When oxidized by means of chromic acid, pyrrole is converted into the imide of maleic acid:



$$\begin{array}{l}CH=CH\diagdown\\ |\qquad\qquad\ \ >NH\\ CH=CH\diagup\end{array} + 3O \rightarrow \begin{array}{l}HC-CO\diagdown\\ \|\qquad\qquad\ >NH\\ HC-CO\diagup\end{array} + H_2O$$

Pyrrole Imide of Maleic acid

(5) When reduced by means of zinc and glacial acetic acid, pyrrole yields dihydropyrrole or **pyrroline**, the two hydrogen atoms going to the α- and α′- positions.[1] Further reduction of pyrroline, by means of hydrogen iodide, converts it into tetrahydropyrrole or **pyrrolidine** :



$$\begin{array}{c}HC-CH\\ \|\quad\ \|\\ HC\ \ CH\\ \diagdown\diagup\\ NH\end{array} \xrightarrow{\text{Zinc and acetic acid}} \begin{array}{c}HC=\!=CH\\ |\qquad |\\ H_2C\quad CH_2\\ \diagdown\diagup\\ NH\end{array} \xrightarrow{HI} \begin{array}{c}H_2C-CH_2\\ |\quad\ |\\ H_2C\ \ CH_2\\ \diagdown\diagup\\ NH\end{array}$$

Pyrrole Pyrroline Pyrrolidine

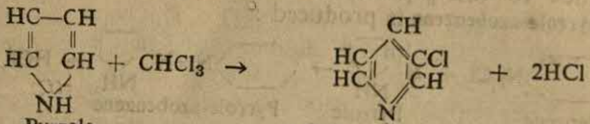
Whereas pyrrole itself is a weak base, pyrroline and, even to a greater degree, pyrrolidine possess strongly basic properties. This is in accord with the general rule. The hydrogenation of an aromatic nitrogen compound is always accompanied by a decided increase in basic properties.

---

[1] This is another example of 1,4-addition in compounds containing conjugated double bonds.

Pyrroline, like the partial reduction products of benzene derivatives, behaves as an unsaturated compound, and, unlike pyrrole, gives addition products with halogens.

(6) When pyrrole is heated with chloroform in the presence of sodium ethoxide, the pyrrole ring gets transformed into the pyridine ring, **β-chloropyridine** being produced :



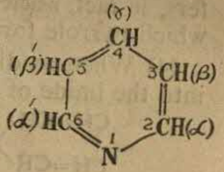
Pyrrole β-Chloropyridine

Test. The vapour of pyrrole imparts a crimson coloration to a pine splint moistened with hydrochloric acid. The colour is due to the formation of an amorphous substance called **pyrrole red.** This test, which is also given by derivatives of pyrrole, was discovered by Runge in 1834.

II. PYRIDINE AND ITS DERIVATIVES

7. The pyridine ring consists of five carbon atoms and one nitrogen atom. The various positions of the substituents are numbered or lettered as given in the margin. The monosubstitution products of pyridine, like the disubstitution products of benzene, exist in three forms, while the disubstitution products occur in six or ten different forms, according as the substituents are similar or dissimilar.

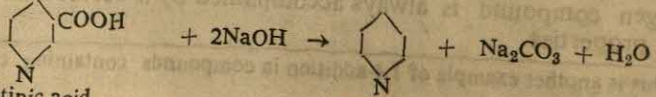
Many of the derivatives of pyridine occur in nature, and belong to the important class of compounds called *alkaloids* (chap. 56).



8. Pyridine.—Pyridine is formed during the destructive distillation of various nitrogenous organic compounds. Hence, it occurs in coal-tar and in bone-oil.

Preparation. (1) Pyridine is isolated from *light oil* of the coal-tar distillation industry and from bone-oil. In either case, the oil is treated with dilute sulphuric acid, which absorbs the pyridine bases. The acid layer is removed and decomposed with sodium carbonate, when the pyridine bases separate out as a dark-brown oil. From this, the pyridine is recovered by fractional distillation.

(2) In the laboratory, a pure sample of pyridine may be readily obtained by distilling *nicotinic acid* (pyridine-β-carboxylic acid) with soda-lime :

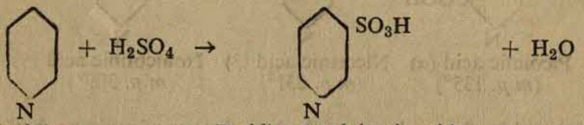


Nicotinic acid pyridine

Properties. *Physical.* (1) Pyridine is a colourless, mobile liquid having a characteristic unpleasant odour, reminiscent of tobacco-smoke. It is miscible with water in all proportions.

(2) *Properties of a Tertiary Amine.* Pyridine, like aliphatic tertiary amines, is basic in nature. It is perfectly miscible with water, and the solution has a faintly alkaline reaction. It combines with acids to form salts such as pyridinium chloride, $(C_5H_5NH)Cl$, and with chloroplatinic acid it forms a sparingly soluble platinichloride, $(C_5H_5NH)_2PtCl_6$. Like other tertiary amines, pyridine directly combines with methyl iodide to give a quaternary ammonium salt, methylpyridinium iodide $(C_5H_5NCH_3)I$. This, on being warmed with solid KOH, gives the quaternary ammonium hydroxide $(C_5H_5NCH_3)OH$, which possesses a most offensive and characteristic odour. The reaction is utilized as a test for pyridine.

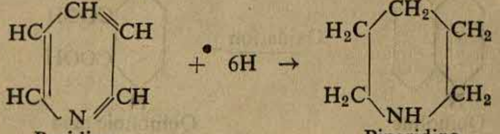
(3) *Properties of a Ring Compound.* Pyridine is remarkably stable, being unattacked by boiling nitric acid or chromic acid. It forms substituted derivatives far less readily than benzene. It yields sulphonic acid derivatives only at very high temperatures, the substituent group entering the β-position:



Pyridine Pyridine-β-sulphonic acid

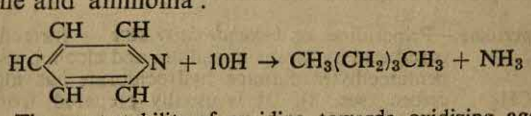
Pyridine can be chlorinated and brominated, but the reactions take place with difficulty. Iodo-derivatives of pyridine are unknown. Nitrous acid has *no* effect on pyridine.

(4) *Reduction.* (*a*) When reduced with sodium and alcohol, it gives the secondary base *piperidine* :

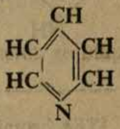


Pyridine Piperidine

(*b*) Energetic reduction with hydrogen iodide at 300° produces normal pentane and ammonia :



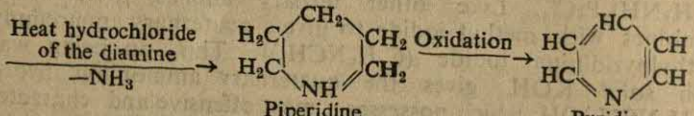
Constitution. The great stability of pyridine towards oxidizing agents (such as $KMnO_4$, H_2CrO_4, HNO_3 etc.), its reaction with sulphuric acid to give sulphonic acids, and the action on chlorine and bromine to give chloro and bromo derivatives (and not addition compounds) prove beyond doubt that pyridine, like benzene, possesses a *ring structure*. The molecular formula, C_5H_5N leads one to think that in pyridine one of the trivalent CH groups of the benzene ring has been replaced by a nitrogen atom. Hence the structure of pyridine may be represented as shown in the margin.



The above view of the constitution of pyridine is supported by its synthesis from allyl bromide given below :

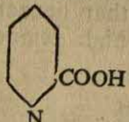
$$\underset{\text{Allyl bromide}}{CH_2{=}CH.CH_2Br} \xrightarrow{+HBr^1} \underset{\text{Trimethylene dibromide}}{BrCH_2\ CH_2.CH_2Br} \xrightarrow[\text{alcoholic KCN}]{\text{Heat with}}$$

$$\underset{\text{Trimethylene dicyanide}}{CN.CH_2.CH_2.CH_2CN} \xrightarrow{H} \underset{\text{Pentamethylenediamine}}{NH_2.CH_2.CH_2.CH_2.CH_2.CH_2.NH_2}$$

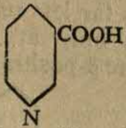


Piperidine Pyridine

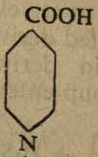
9: Pyridinecarboxylic Acids.—All the three pyridinemonocarboxylic acids are known :



Picolinic acid (α)
(*m.p.* 135°)



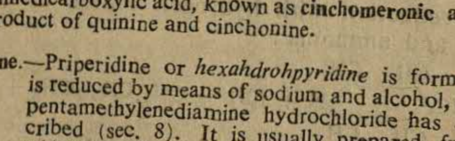
Nicotinic acid (β)
(*m.p.* 231°)



Isonicotinic acid (γ)
(*m.p.* 309°)

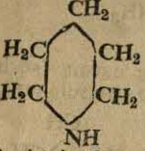
They are formed by the oxidation of the homologues of pyridine having one side-chain. Nicotinic acid is produced by the oxidation of the alkaloid nicotine ; hence the name.

Of the six pyridinedicarboxylic acids, the best known is the **quinolinic acid.** This is the α,β-compound, and is produced by the oxidation of quinoline with potassium permanganate :



Quinoline Quinolinic acid

The β,γ-pyridinedicarboxylic acid, known as **cinchomeronic** acid, is obtained as a degradation product of quinine and cinchonine.



10. Piperidine.—Priperidine or *hexahdrohpyridine* is formed when pyridine is reduced by means of sodium and alcohol, its synthesis from pentamethylenediamine hydrochloride has already been described (sec. 8). It is usually prepared from black pepper which contains the alkaloid **piperine.** The latter, when boiled with alkalis, gets decomposed, yielding piperic acid.

Well powdered black pepper is extracted with alcohol, the liquid is filtered, and the alcohol evaporated off. The residue is distilled with

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[1] The bromine atom already present in the allyl bromide molecule makes the newly entering bromine atoms take up a position *further away* from itself.

potash and the distillate, after neutralization with hydrochloric acid, is evaporated to dryness. The residue from the latter process is extracted with hot alcohol to dissolve out the piperine hydrochloride, while ammonium chloride, which is always present, is left undissolved.

The alcoholic solution is filtered, evaporated to dryness, and the residue distilled with solid potassium hydroxide, when piperidine passes over.

Properties. (1) Piperidine is a colourless liquid, having a characteristic ammoniacal odour (compare aliphatic amines) and boiling at 105°.

(2) It is a far stronger base than pyridine (compare pyrrolidine) being comparable in this respect with aliphatic amines.

(3) It possesses the properties of a secondary amine, and, when treated with nitrous acid, gives **nitrosopiperidine**, an oily liquid boiling at 218°. Further, it reacts with methyl iodide, yielding **N-methylpiperidine**[1], $C_5H_{10}N.CH_3$.

(4) When heated with concentrated sulphuric acid at 300°, piperidine gets oxidized to pyridine.

(5) When piperidine is oxidized by means of hydrogen peroxide, the ring is broken between the nitrogen atom and an adjacent carbon atom, with the formation of **δ-aminovaleraldehyde**, $NH_2CH_2CH_2CH_2CH_2CHO$.

QUESTIONS

1. What do you understand by a heterocyclic compound? Mention three instances of such compounds; give their structural formulae, and discuss their constitutions. *(Punjab, B.Sc., 1934)*

2. How does pyrrole occur in nature? Give any two methods for its synthesis. Describe its chemical properties, indicating how far it resembles a phenol and an aromatic amine. *(Poona, B.Sc., Second Year, 1961)*

3. Write a clear and concise note on Furan. *(Rajasthan, B.Sc., 1961)*

4. How is pyridine obtained? Give its chemical properties. How was its structure established? State exactly how you would obtain picolinic acid starting from pyridine. *(Nagpur, B.Sc., 1952)*

5. How is pyridine obtained on a large scale? How would you proceed to prepare picolinic acid from pyridine?

Discuss the constitution of pyridine and show how the given structure is justified by the chemical behaviour of pyridine. *(Punjab, B.Sc., 1955)*

6. Outline the properties of pyridine, comparing and contrasting them with those of benzene and a tertiary aliphatic amine and also outline the evidence upon which the formula of pyridine rests. *(Rajasthan, B.Sc., 1961)*

7. Write a detailed account of preparation, properties and constitution of pyridine. *(Jammu & Kashmir, B.Sc., 1960)*

8. Describe two methods for the synthesis of pyridine. Compare and contrast its chemical behaviour with that of benzene. *(Venkateswara, B.Sc., 1960)*

9. Discuss the constitution of pyridine. In what respects does pyridine resemble and differ from benzene? *(Punjab, B.Sc., 1963)*

10. What are heterocyclic compounds? Compare and contrast benzene and pyridine in their properties. *(Delhi, B.Sc., 1958)*

11. Describe a convenient method for the preparation of pyrrole and compare and contrast its properties with those of phenol and pyridine. *(Utkal, B.Sc., 1960)*

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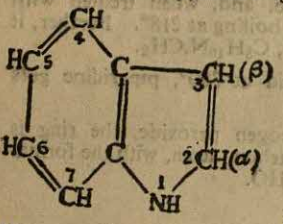
[1] The letter N attached to a substituent indicates that the substituent is linked to the nitrogen atom.

CHAPTER FIFTY-FIVE

HETEROCYCLIC COMPOUNDS CONTAINING CONDENSED NUCLEI

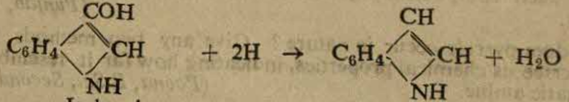
1. Indole (*Benzopyrrole*).—The molecule of indole contains a benzene ring condensed with a pyrrole ring. The positions of substituents in the indole molecule are indicated as in the formula given in the margin.



The importance of indole lies chiefly in its being the parent substance of indigo. Indole and three of its derivatives (*skatole, skatolecarboxylic acid* and *tryptophane*) occur among the putrefaction products of proteins.

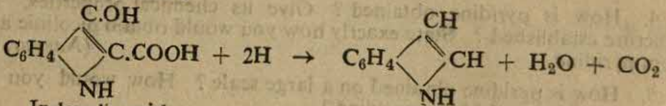
Occurrence. Indole is present in coal-tar, in faeces, and in the oils of jasmine flower, and orange blossom. In spite of its disagreeable odour, it finds application in perfumery.

Preparation. (1) Indole is best prepared by the reduction of indoxyl or indoxylic acid in alkaline solution :



Indoxyl
(β-Hydroxyindole)

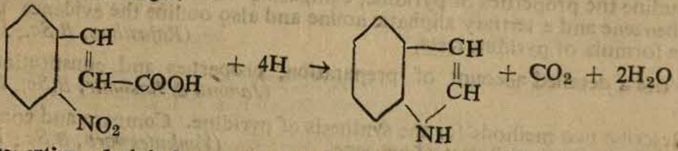
Indole



Indoxylic acid
(Indoxyl-α-carboxylic acid)

Indole

(2) Indole may also be prepared by heating *o*-nitrocinnamic acid with caustic potash and iron filings :

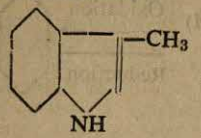


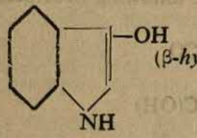
Properties. Indole forms white leaflets (*m.p.* 52°) having a disagreeable faecal odour. After being carefully purified, however, it may be mixed in minute quantities other perfumes with the surprising result that the mixture acquires the fragrance of fresh flowers ; **hence the use of indole in artificial jasmine and neroli oils.**

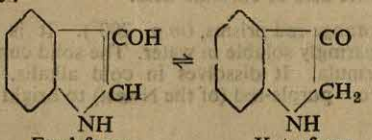
Indole is volatile in steam, and is soluble in hot water and organic solvents.

In chemical character, indole resembles pyrrole ; it possesses weakly basic properties, is resinified by acids and gives a red colour to a pine splint moistened with hydrochloric acid. When oxidized with ozone, it yields indigo.

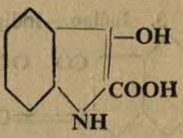
2. Derivatives of Indole :—

Skatole.  (β-*methylindole*), is present in human faeces, and is the chief cause of the repulsive odour. It crystallizes in colourless plates, (*m p.* 95°).

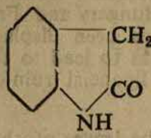
Indoxyl,  (β-*hydroxyindole*), occurs as the glucoside *indican* in the indigo plant and as the potassium salt of indoxylsulphonic acid, in the urine of mammals. It can be readily prepared by decomposing indoxylic acid with hot water. It forms bright yellow crystals, (*m.p.* 85°). In alkaline solution, it is readily oxidized, even by atmospheric oxygen, into indigo (sec. 3). It exhibits tautomerism of the keto-enol type :



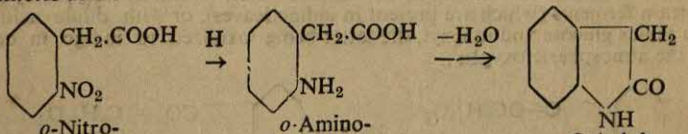
Enol-form Keto-form



Indoxylic acid (*indoxyl-α-carboxylic acid*) is of interest as an intermediate product in the manufacture of indigo. When heated with water, it loses carbon dioxide, and yields indoxyl. On being oxidized, it gives indigo.

Oxindole, , is the inner anhydride of *o*-aminophenylacetic acid.

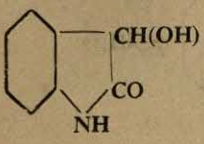
It is produced by the reduction of *o*-nitrophenylacetic acid with tin and hydrochloric acid :



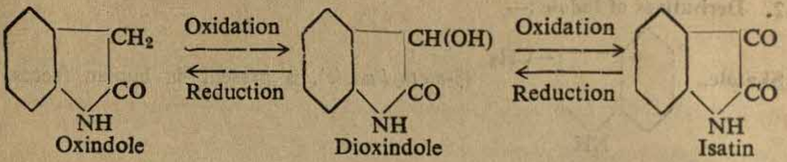
o-Nitro-phenylacetic acid | *o*-Amino-phenylacetic acid | Oxindole

It may be obtained by the reduction of isatin (see below).

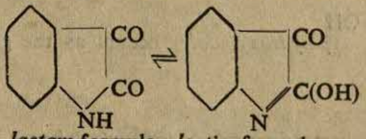
Oxindole crystallizes in colourless needles, melting at 120°. When subjected to oxidation, it gives dioxindole.



Dioxindole, is the inner anhydride of *o*-aminomandelic acid. It is formed in an analogous manner to oxindole by the reduction of *o*-nitro-mandelic acid. It forms colourless prisms which melt at 183°. On reduction it yields oxindole, and on oxidation isatin :—



Isatin is the inner anhydride of *o*-aminobenzoylformic acid. It is a tautomeric substance, and may react according to either of the following structures:

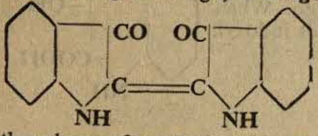


lactam formula *lactim* formula

As mentioned above, isatin may be obtained by the oxidation of dioxindole or oxindole, into which it reverts on reduction. It is also formed by the oxidation of indigo by means of nitric acid or chromic acid.

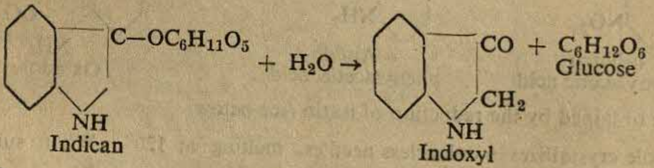
Isatin crystallizes in orange-red prisms, (*m.p.* 200°). It is readily soluble in alcohol and ether, but sparingly soluble in water. The solid compound is supposed to possess the lactam formula. It dissolves in cold alkalis, and the solution, if dilute, changes colour from purple-red (of the N-salt) to bright yellow (of the O-salt).

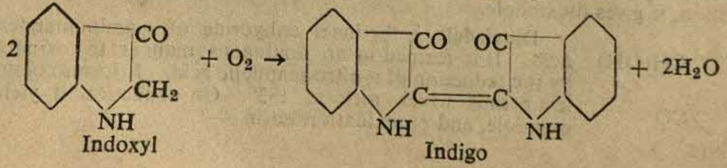
Isatin condenses with thiophene, yielding the blue dye-stuff **indophenine.**



3. **Indigo.**—Indigo, or **indigotin**, is the chief constituent of natural indigo, which is one of the most important dye-stuffs. From the very early times, indigo has been prepared from the indigo plant (*Indigofera-tinctoria*) grown in Bengal, Java, China, and Japan. It is also obtained from woad (*Isatis tinctoria*) grown in Hungary and France. With the advent of synthetic indigo the natural product has been displaced to a very large extent, and the competition was so keen as to lead to the abandonment of many indigo plantations, and the consequent financial ruin of their proprietors.

Preparation of Natural Indigo. Indigo occurs in the leaves of the plant, not as such, but in the form of **indican**, the glucoside of indoxyl, and is a crystalline substance extractable from the leaves with hot water. When hydrolysed by means of certain ferments (which are present in indigo leaves), or with dilute acids, indican yields glucose and indoxyl, the latter being oxidized to indigo in contact with the atmospheric oxygen :

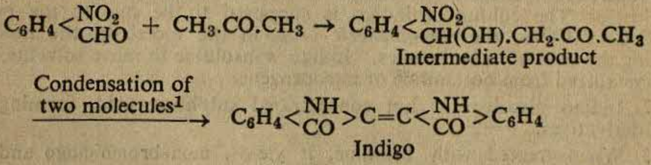




The plants are cut down shortly before flowering, and are macerated with water at 25° to 30° in large vats made of stone. The indican undergoes fermentation under the influence of enzymes present in the leaves, with the formation of indoxyl and glucose. When the fermentation is over (10 to 12 hours), the liquid, which contains ammonia in addition to indoxyl, is run into another set of vats placed at a lower level. Here it is churned with air, whereby indoxyl gets oxidized to indigo, the latter separating as blue flakes. When the oxidation is complete the indigo is allowed to settle, and is washed free from soluble matter. It is then boiled with water, filtered, and finally dried.

The natural indigo, obtained as above, consists of blue lumps containing 60 to 80 per cent of *indigotin*, the rest being *indigo red*, *indigo brown*, "indigo gelatin", and ash. These substances may be removed by successive treatment of the natural product with water, dilute acetic acid, caustic soda and alcohol.

Synthesis of Indigo. The great industrial importance of indigo naturally tempted many chemists to discover synthetic process for its manufacture. As the result of laborious research by Baeyer and his pupils the constitution of indigo was established in about 1880. Baeyer succeeded in synthesising indigo by a number of methods, one of which consists in mixing a solution of *o-nitrobenzaldehyde* in acetone with a dilute solution of alkali, when a precipitate of indigo is gradually formed.



$$C_6H_4<\begin{matrix}NO_2\\CHO\end{matrix} + CH_3.CO.CH_3 \rightarrow C_6H_4<\begin{matrix}NO_2\\CH(OH).CH_2.CO.CH_3\end{matrix}$$

Intermediate product

$$\xrightarrow[\text{two molecules}^1]{\text{Condensation of}} C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C=C<\begin{matrix}NH\\CO\end{matrix}>C_6H_4$$

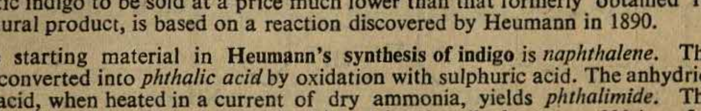
Indigo

This and several others of the proposed methods were, however, found to be unsuitable for the synthetic manufacture of indigo at a sufficiently low cost to compete with the natural product.

(1) The method that has proved a commercial success, and which enables synthetic indigo to be sold at a price much lower than that formerly obtained for the natural product, is based on a reaction discovered by Heumann in 1890.

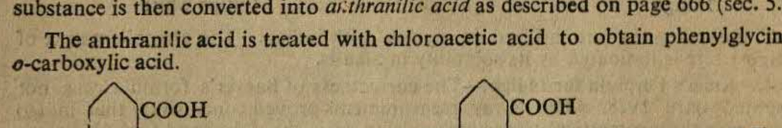
The starting material in **Heumann's synthesis of indigo** is *naphthalene*. This is first converted into *phthalic acid* by oxidation with sulphuric acid. The anhydride of the acid, when heated in a current of dry ammonia, yields *phthalimide*. This substance is then converted into *anthranilic acid* as described on page 666 (sec. 5.)

The anthranilic acid is treated with chloroacetic acid to obtain phenylglycine-*o*-carboxylic acid.



Anthranilic acid Phenyl-glycine-*o*-carboxylic acid

which, when fused with potash yields *indoxyl*, indoxylic acid being formed as the intermediate product :



Phenyl-glycine-*o*-carboxylic acid Indoxylic acid Indoxyl

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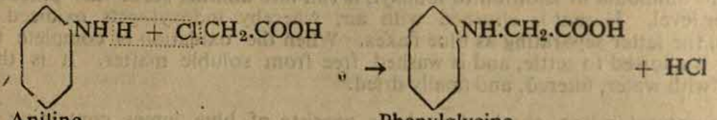
[1] In this reaction, two molecules of acetic acid and two of water are eliminated.

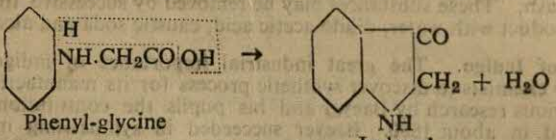
The fused mass, containing indoxyl, is dissolved in water and a stream of air is passed through the alkaline liquid, when indigo is precipitated (compare preparation of natural indigo).

(2) Another synthesis carried out on the large-scale is as follows : Aniline is treated with monochloroacetic acid, when *phenylglycine* is obtained :



Aniline Phenylglycine

Phenylglycine is fused with alkali at 180° to 240°, when indoxyl is produced,



Phenyl-glycine Indoxyl

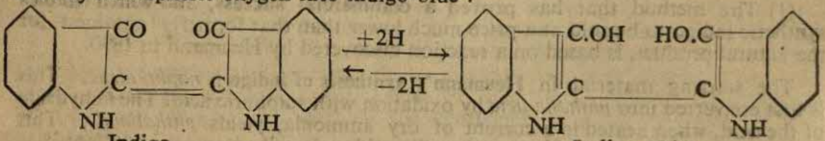
which may be converted into indigo, as in the above synthesis.

Properties of Indigo. (1) Indigo is a dark blue powder with a copper-like lustre The colour of indigo is supposed to be due to the presence of —CO.C=C.CO—, the *chromophoric group* in the molecule, the imido groups playing the part of auxochromes. Indigo is insoluble in most solvents, but may be crystallized from hot aniline or nitrobenzene.

(2) Indigo dissolves in hot concentrated sulphuric acid, forming sulphonic acid derivatives.

(3) When treated with bromine, it yields, **monobromoindigo** and **dibromo-indigo**, which are also used as dyes.

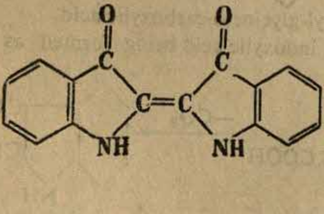
(4) When subjected to reduction in aniline solution, indigo takes up two atoms of hydrogen yielding **indigo white** or **di-indoxyl**, which is readily re-oxidized, even by atmospheric oxygen into indigo-blue :



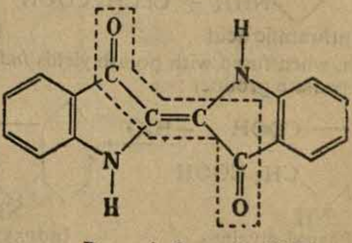
Indigo Indigo white

These reactions are utilized in dyeing with indigo. The phenolic nature of indigo-white is indicated by its solubility in alkalis.

4. Kuhn's Formula for Indigo.—The correctness of Baeyer's formula was not disputed until 1928, when X-ray measurements proved conclusively that indigo must have the symmetrical *trans* configuration, as in the right-hand formula below:



Baeyer's formula (1883)
(*cis* configuration, now
discarded)



Baeyer's formula (1928)
(*trans* configuration)

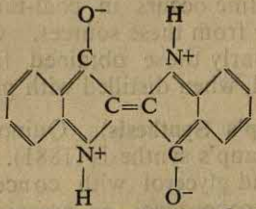
Kuhn pointed out that in arriving at the correct formulation of indigo, the undermentioned facts must all be taken into consideration :—

1. The *trans* configuration, as revealed by the X-ray measurements.

2. As shown by dotted lines, the Baeyer formula (*trans* form) contains a conjugated system of double bonds similar to that in *para* quinones (which are much paler in colour), and does not therefore accord with the strong colour that indigo possesses.

3. Indigo has certain special properties, which the classical formula does not explain. It has a high melting point (390°C) ; is red in the vapour state and also when dissolved in non-polar solvents. In polar solvents (*e.g.*, xylene), the colour is deep blue and the molecular weight has twice the normal value.

Taking into account all these facts, Kuhn has suggested the following **tetrapolar-ion formula** for indigo :—



Kuhn's tetrapolar-ion formula for indigo.

The formula explains the *trans* orientation of the indigo molecule, as the opposite charges on the nitrogen and oxygen atoms in the two halves would attract each other. The conjugation of double bonds is more extensive than in the Baeyer formula, and hence more in accord with the intense colour that indigo possesses. The heteropolar character also contributes towards the intensification of colour as in hydrocarbon picrates (which must be regarded as dipolar complexes). The double molecules present in blue solutions are, according to Kuhn, due to one molecule getting superimposed on another in such a way that the four charges of the first molecule are attracted by opposite charges of the second, with the consequent intensification of colour.

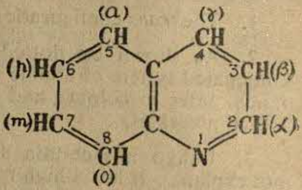
5. **Dyeing with Indigo.**—Indigo is a **vat-dye,** and is applied to cloth as follows : Finely-divided indigo is suspended in water, and reduced. This may be effected by **fermentation** in the presence of lime or soda, a process that has been in use from the very early times, and still considered the best for woollen goods. Alternatively, chemical reducing agents may be employed, such as glucose, zinc-dust, ferrous sulphate, stannous chloride or sodium hydrosulphite. The method of reduction employed in a particular case depends upon the nature of the material to be dyed. The **hydrosulphite vat** is the best one to use for cotton. It is prepared by mixing zinc dust with a solution of sodium bisulphite, and, when the latter has been completely reduced to sodium hydrosulphite, $Na_2S_2O_4$, adding milk of lime. The clear liquid is run off from the precipitate ($CaSO_3$, etc.), sodium hydroxide solution and indigo paste are added and the mixture is warmed to 60°. A concentrated solution of indigo white ("stock vat") is thus obtained, from which the dyeing vats of proper concentration are prepared by dilution with water.

The cloth to be dyed is steeped in the solution of indigo-white prepared by a suitable method. It is then exposed to air, whereby the indigo white gets oxidized to indigo, which, being insoluble, remains fixed within the fabric.

Indigo imparts a bright blue colour, which is very fast to light and washing.

6. **Quinoline.**—Quinoline may be regarded as α, β-benzopyridine or as naphthalene in which one of the CH groups in the α position is replaced by a nitrogen atom. The position of substituents in

the quinoline molecule is usually indicated by numbering the substituents as shown in the formula. Alternatively, they are designated as α-, β- and γ- in the pyridine ring and as *ortho-*, *meta-*, *para-*, and *anna-* (*o-*, *m-*, *p-*, and *a-*) in the benzene ring.



The number of isomeric substitution products in the case of quinoline is very large. Thus, the monosubstitution-products exist in seven and disubstitution products containing similar substituents in twenty-one different forms.

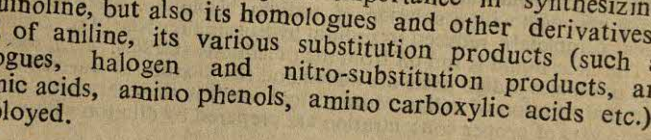
Occurrence.—Quinoline occurs in coal-tar and bone-oil, but is difficult to obtain pure from these sources. Certain naturally occurring alkaloids, particularly those obtained from cinchona, contain quinoline nucleus, and, when distilled with potash, yield quinoline.

Preparation (Skraup's Synthesis). Quinoline is almost exclusively prepared by Skraup's synthesis (1881). This consists in heating a mixture of aniline and glycerol with concentrated sulphuric acid (dehydrator) and nitrobenzene[1] or arsenic acid (oxidizer). The reaction is supposed to take place as follows :

Under the influence of concentrated sulphuric acid, glycerol loses two molecules of water, yielding acrolein.

$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} \xrightarrow{-2H_2O} \underset{\text{Acrolein}}{CH_2{=}CH.CHO}$$

This, like benzaldehyde, condenses[2] with aniline, producing acrolein-aniline which is then oxidized to quinoline :



Aniline Acrolein Acrolein-aniline Quinoline

Skraup's synthesis is of great importance in synthesizing not only quinoline, but also its homologues and other derivatives : as, instead of aniline, its various substitution products (such as its homologues, halogen and nitro-substitution products, amino-sulphonic acids, amino phenols, amino carboxylic acids etc.) may be employed.

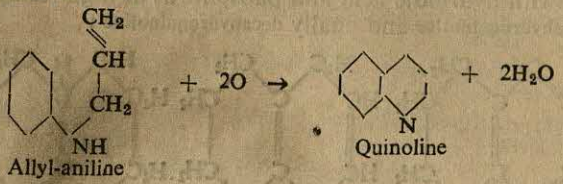
Other Syntheses. In addition to Skraup's synthesis, described above, quinoline has been synthesized by a variety of methods, which clearly indicate its **constitution.**

---

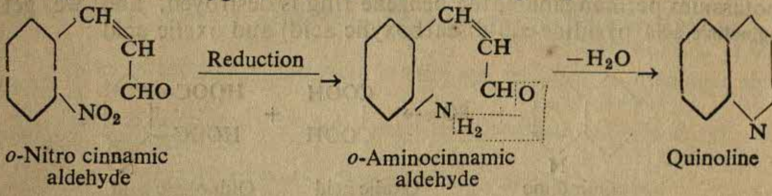
[1] Nitrobenzene acts as an oxidizing agent, being itself reduced to aniline.

[2] The condensation of acrolein with aniline also occurs under the condensing action of sulphuric acid.

(1) *Konigs' Synthesis.* The first synthesis of quinoline, effected by Konigs in 1879, consists in passing the vapour of allylaniline over red-hot oxide of lead :



(2) *Baeyer and Drewsens' Synthesis.* This synthesis consists in the reduction, in acid medium, of *o*-nitrocinnamic aldehyde. The first stage of the reaction is the reduction of the nitro group to the amino group, the hydrogen atoms of which are then eliminated along with the oxygen atom of the aldehyde group :



Constitution. The constitution of quinoline follows from the synthesis described above. The last one of these clearly proves that quinoline is an *ortho* derivative of benzene. This view of the constitution of quinoline is fully supported by reactions, 2, 3, and 4 given below.

Properties. (1) Quinoline is a colourless, highly refractive, oily liquid, (*b. p.* 240°). It has a pleasant, characteristic odour, and is sparingly soluble in water, readily soluble in alcohol, ether and most other organic solvents.

(2) In chemical properties, quinoline resembles pyridine and possesses the characters of a *tertiary* base. **Quinolinium dichromate,** which is obtained by adding potassium dichromate to a solution of quinoline in dilute hydrochloric acid, is sparingly soluble, and forms yellow needles melting at 165°. With methyl iodide quinoline gives *N*-**methylquinolinium iodide,** $[C_9H_7N(CH_3)]$ I, which melts at 133°.

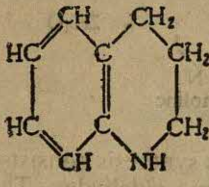
(3) Quinoline possesses a distinctly aromatic character, and can be directly sulphonated or nitrated, **substitution occurring ordinarily in the benzene nucleus.** Thus the first products formed on nitration are 5- and 8-**nitroquinolines,** which on further nitration, give, 5,7- and 6,8-dinitroquinolines.[1]

(4) Like other aromatic compounds quinoline can be reduced, the pyridine-ring undergoing hydrogenation in preference to the

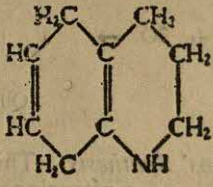
---

[1] That is, the second nitro-group in each case takes up the *m*-position with respect to the nitro-group already present (Crum-Brown and Gibson rule).

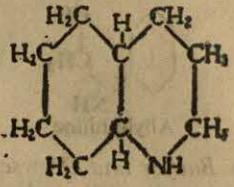
benzene ring. Thus, when treated with zinc and hydrochloric acid, quinoline yields **tetrahydro quinoline,** which, on more energetic reduction with hydriodic acid and phosphorus at high temperatures, yields **hexahydroquinoline** and finally **decahydroquinoline :**



Tetrahydro-
quinoline

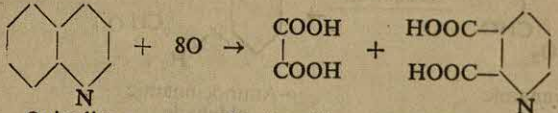


Hexahydro-
quinoline

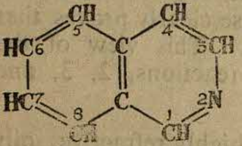


Decahydro-
quinoline

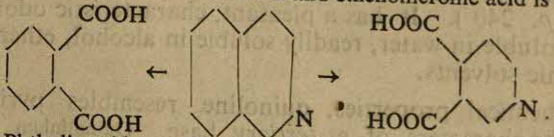
(5) When quinoline is oxidized with an alkaline solution of potassium permanganate, the benzene ring is destroyed, and we get **quinolinic acid** (pyridine-α,β-discarboxylic acid) and oxalic acid :



Quinoline Oxalic acid Quinolinic acid



7. **Isoquinoline.**—Isoquinoline is β,γ-benzopyridine, the positions of the substituents in the molecule being indicated as given in the formula in the margin. This constitution is proved by various syntheses of isoquinoline and its behaviour on oxidation. When treated with potassium permanganate, the benzene and the pyridine nuclei are attacked, and a mixture of phthalic acid and cinchomeronic acid is obtained :



Phthalic acid Isoquinoline Cinchomeronic acid

Isoquinoline occurs in coal-tar quinoline, from which it may be separated in the form of sparingly soluble sulphate. It is a colourless liquid (*m.p.* 23° and *b.p.* 240°), and closely resembles quinoline in physical properties.

The chief interest of isoquinoline lies in the fact that papaverine, narcotine and certain other alkaloids are derived from it.

QUESTIONS

1. Describe the preparation, chief properties and industrial uses of indole. Why is indole an important compound ? Give the constitutional formulae of indole and any four of its derivatives.

2. Discuss the constitution of Quinoline. (*Poona, B.Sc., 1953*)

3. How would you prepare indigo and establish its constitution ? (*Punjab, B.Sc., 1950*)

4. How is indigo prepared ? Give its properties and uses. (*Punjab, B.Sc., 1954*)

5. How have the structures of quinoline and isoquinoline been established? Give methods for the synthesis of quinoline and isoquinoline ring systems.
(Bombay, B.Sc., 1950)

6. Give an account of the chemistry of indigo including its commercial preparation.
(Bombay, B.Sc., 1952)

7. Describe Skraup's synthesis of quinoline. Discuss fully the constitution of quinoline.
(Delhi, B.Sc., 1955)

8. Outline the steps involved in the synthesis of :—

(*a*) Glycerine from propylene, (*b*) indigo from naphthalene, (*c*) *m*-nitroaniline from benzene and (*d*) quinoline from aniline. *(Andhra, B.Sc., 1956)*

9. How does indigo occur in nature and how is it obtained from these sources? Describe its synthesis. How can it be made available for dyeing cotton and wool?
(Jammu and Kashmir, B.Sc., 1957)

10. How is indigo obtained? Discuss the evidence for the structure assigned to it and give its commercial synthesis. Describe its use as a dye on fabrics.
(Gujarat, B.Sc., 1957)

11. How can quinoline be prepared? Give the reactions of quinoline and discuss its formula.
(Aligarh, B.Sc., 1958)

12. Describe the reactions which helped to determine the constitution of quinoline. Give its synthesis.
(Poona, B.Sc., 1960)

13. (*a*) Compare the properties of pyridine with those of benzene.

(*b*) Discuss the structure of pyridine. *(Lucknow, B.Sc., 1960)*

14. Give an account of the general methods for the synthesis of quinoline and isoquinoline. Mention their properties. *(Karnatak, B.Sc., 1961)*

15. Give an account of the chemistry of isoquinolines. *(Jadavpur, B.Sc., 1961)*

16. Discuss the constitution of pyridine. *(Lucknow, B.Sc., 1962)*

17. Discuss the constitution of indigo, and give its laboratory and commercial synthesis.
[*Bombay, B.Sc., Chemistry (Subs.), 1962*)

CHAPTER FIFTY-SIX

ALKALOIDS

1. GENERAL

The name "alkaloid" is given to a group of organic bases of vegetable origin, in which at least one nitrogen atom is present as a member of a heterocyclic ring.[1] About two hundred alkaloids are known, some of which possess important physiological and therapeutic properties.

1. **Occurrence.**—Alkaloids occur throughout the vegetable kingdom, but they are very abundant in certain orders of the dicotyledonous plants, such as *Papaveraceae*, *Solanaceae*, *Ranunculaceae*. The alkaloids present in a plant may be detected in all parts of it, but as a rule they accumulate in the fruit and seeds and sometimes also in the bark. Usually, more than one alkaloid occurs together in one plant. Thus, opium contains about 20 known alkaloids. The alkaloids present in one plant are generally closely related in chemical constitution.

Alkaloids do not exist in plants in the free state, but as salts, sometimes of the common plant acids, such as malic or citric, and sometimes of special acids, such as quinic acid in the alkaloids of the cinchona bark, and meconic acid in those of the morphine group.

2. **Extraction.**—There are three different methods of extracting alkaloids from plants :—

(1) The finely-divided material is lixiviated with water that has been acidified with hydrochloric or sulphuric acid. The lixiviation is effected in a **percolator**—a conical vessel tapering towards the bottom. A layer of flint or glass wool is placed at the bottom of the percolator to keep the material to be extracted in position. The mineral acids liberate the alkaloids from their salts with organic acids, and convert them into hydrochlorides or sulphates, which pass into solution together with the colouring matter, carbohydrates and other soluble constituent of the plant. The extract is strongly alkalified, whereby the alkaloid is set free. If insoluble, it is separated by filtration ; if soluble, it may be extracted from the aqueous solution with ether or chloroform.

(2) The macerated vegetable matter is treated with aqueous alkali and the alkaloid extracted with a suitable solvent. The solution is treated with dilute acid, when the alkaloid in the form of a salt passes into the aqueous layer, and is separated.

(3) If the alkaloid to be extracted is volatile, *e.g.*, coniine or nicotine, it may be recovered by treating the solution or finely-divided raw material with alkali and distilling in steam.

3. **General Properties.**—(1) Most of the alkaloids are crystalline solids which cannot be distilled ; a few only, such as *coniine* and *nicotine*, are liquids, and

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[1] Sometimes the term "alkaloid" is extended to include certain aliphatic compounds containing nitrogen, *e.g.*, betain, choline, caffeine, and theobromine In its restricted sense, however, the term is applied only to compounds containing the pyridine nucleus.

volatilize without decomposition. A great majority are optically active (showing in most cases levorotation, possess a bitter taste, and exert a marked physiological action on the animal organism. Most of them are insoluble in water, more or less soluble in ether or chloroform, and readily soluble in alcohol.

(2) Being basic in nature, they dissolve in acids, yielding salts that may be readily crystallized. The hydrochlorides of alkaloids, like those of other organic bases, form double chlorides with the chlorides of platinum, gold and mercury.

(3) Certain substances, called **alkaloid reagents**, precipitate most of the alkaloids from aqueous or acidic solutions. Examples of such reagents are tannic acid, picric acid, phosphomolybdic acid, phosphotungstic acid, and potassium mercuri-iodide. Strong tea acts as an antidote in cases of poisoning by alkaloids, the tannin present in the tea precipitating the alkaloid and rendering it harmless.

(4) Certain alkaloids, such as quinine, strychine and brucine, give characteristic colour reactions, which are very valuable for their identification.

4. **Constitution of Alkaloids.**—The determination of the constitution of an alkaloid involves : (1) the identification of the various groups present in the molecule, such as OH, OCH_3, CH_3 and CO, and (2) the determination of the particular ring-system in union with these groups. The following are the chief methods employed in the elucidation of these points.

(1) *Hydrolysis.* When submitted to hydrolysis by means of acids or alkalis, many of the alkaloids decompose into (*i*) a characteristic alkaloidal constituent containing nitrogen, and (*ii*) a nitrogen-free component, usually a carboxylic acid. Atropine, for example, yields tropine and tropic acid.

(2) *Degradation.* Another method of determining the particular ring system present in an alkaloid consists in distilling it with zinc-dust, alkali, or some other vigorous reagent, when the parent heterocyclic compound is obtained. Thus, cinchonine when distilled with caustic soda yields quinoline, showing that this alkaloid molecule contains the quinoline ring.

(3) *Oxidation.* When submitted to oxidation, an alkaloid may be attacked at an ethylenic bond $>C=C<$, a carbinol group, $>CH(OH)$, or at a methylimino group, $>N(CH_3)$.

The products obtained by the oxidation of an alkaloid by means of potassium permanganate and other reagents, therefore, give a valuable information as regards the constitution of the alkaloid.

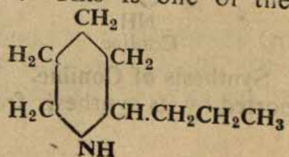
(4) *Exhaustive Methylation.* The method of exhaustive methylation has been of frequent use in the study of the constitution of alkaloids.

(5) *Determination of Methoxyl Groups.* These are estimated by Zeisel's method (page 260).

5. **Classification.**—Alkaloids are classified with reference to the basic compounds from which they are derived, *e.g.*, pyridine, quinoline, isoquinoline, indole, etc. Thus coniine and piperine are the alkaloids of the pyridine group. Similarly, quinine is derived from quinoline, and strychnine from indole ; hence they belong to the quinoline group and the indole group respectively.

II. INDIVIDUAL ALKALOIDS

6. **Coniine,** *α-n-Propyl-piperidine*, $C_8H_{17}N$.—This is one of the very few alkaloids containing no oxygen, and of these it possesses the simplest structure. The chief interest of coniine lies in the fact that it was the first of the alkaloids to be prepared synthetically.



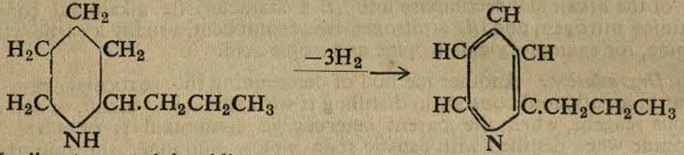
Occurrence and Extraction. The hemlock plant (Conium *maculatum*) contains coniine and a number of other alkaloids related to it. The fruit and seeds of hemlock are particularly rich in these alkaloids, which occur chiefly in combination with malic and caffeic acids.

The extraction of the alkaloids is carried out by steam-distilling the powdered seeds, or the whole plant, with aqueous sodium hydroxide.

Physical Properties. Coniine is a colourless, dextro-rotary liquid having a strong, stupefying odour, and is highly poisonous. It is insoluble in water, and boils at 167°.

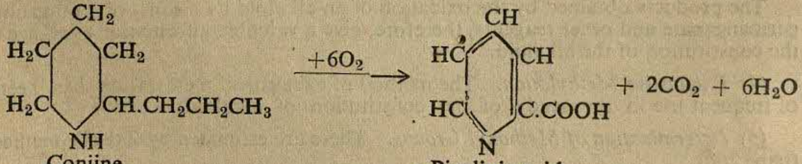
Reactions and Constitution. Coniine, being a strong base, forms salts with acids (*e.g.*, the hydrochloride, $C_8H_{16}NH,HCl$). The following reactions of this alkaloid prove its constitution as **α-propylpiperidine :—**

(1) *Dehydrogenation.* When coniine is heated with silver acetate, or its hydrochloride distilled with zinc dust, we get α-propylpyridine or *conyrine* :—



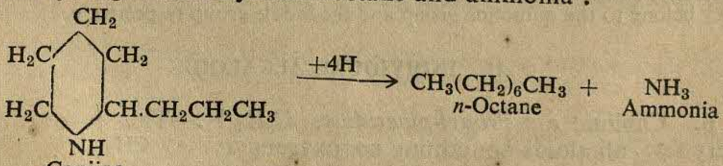
Coniine (α-propylpiperidine) Conyrine (α-propylpyridine)

(2) *Further Oxidation.* Stronger oxidation (*e.g.*, with potassium permanganate) results in the degradation of the base to α-picolinic acid (pyridine-α-carboxylic acid) :—



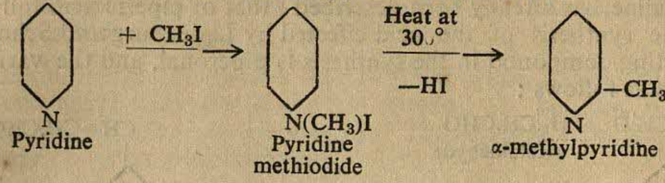
Coniine α-Picolinic acid

(3) *Rupture of the Ring.* Reactions that occur with disintegration of the coniine ring yield derivatives of *n*-octane. Thus, strong heating with hydrogen iodide yields *n*-octane and ammonia :

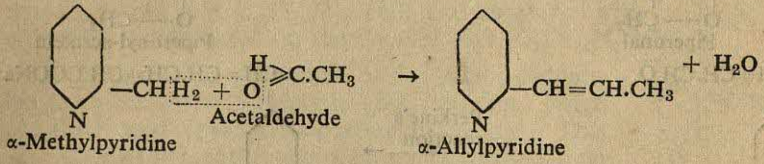


Coniine

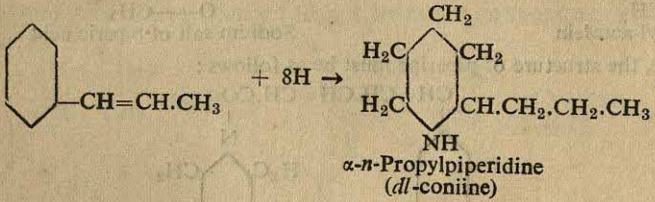
Synthesis of Coniine. The constitution of coniine was fully supported by its synthesis from pyridine (Ladenburg, 1886). The base was first converted into *a*-methylpyridine as follows :



The α-methylpyridine was then heated with paracetaldehyde at 250° in the presence of zinc chloride, when *a*-allylpyridine was formed :



The last-named compound was reduced with sodium and alcohol to coniine :



The *dl*-coniine was separated into its optically active components by fractional crystallization of the tartrates.

7. Piperine, $C_{17}H_{19}NO_3$.—The fruit and seeds of different species of pepper, especially of black pepper (*Piper nigrum*), contain 8 to 9 per cent of piperine. The base can be readily extracted from the black pepper.

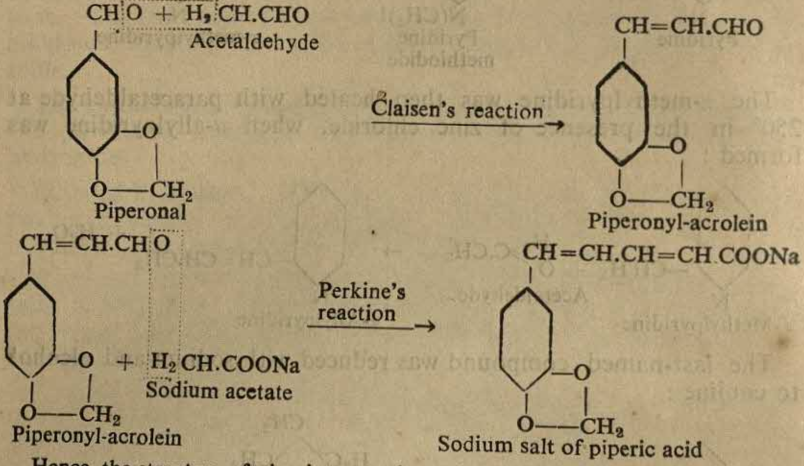
The powdered black pepper is warmed with milk of lime for about 15 minutes. The mixture is evaporated to dryness on a water bath, and the residue is extracted with ether. The crude piperine, obtained by evaporating off the ether, is purified by crystallization from alcohol.

Piperine forms colourless crystals (*m.p.* 128°). It is almost insoluble in water. Piperine is a very weak base, and dissolves in concentrated sulphuric acid, yielding a deep red solution.

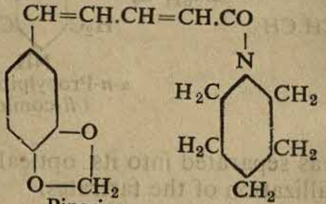
Constitution. When boiled with alkalis, piperine yields piperidine and piperic acid :

$$\underset{\text{Piperine}}{C_{17}H_{19}NO_3} + H_2O \rightarrow \underset{\text{Piperidine}}{C_5H_{11}N} + \underset{\text{Piperic acid}}{C_{12}H_{10}O_4}$$

From this it may be concluded that piperine is a substituted amide of piperic acid in which piperine is the basic constituent. This view is confirmed by the fact that piperine may be synthesized by heating piperidine with the chloride of piperic acid. The constitution of piperidine has already been described ; that of piperic acid follows from the synthesis of the acid effected by Ladenburg and Scholtz. The starting compound in the synthesis is piperonal, and the various steps are as follows :



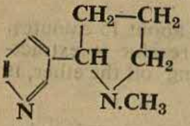
Hence, the structure of piperine must be as follows :



Piperine

Synthesis. From what has been said above it follows that piperine may be synthesized from piperonal and piperidine.

8. Nicotine, 1-*Methyl*-2-β-*pyridylpyrrolidine*, $C_{10}H_{14}N_2$.—



Occurrence. In combination with malic and citric acids, nicotine occurs in the leaves of tobacco (*Nicotiana tobacum*), the quantity varying from 0·6 to 8 per cent. As a rule, the better kinds of tobacco have a smaller nicotine content.

Extraction. Tobacco leaves of high nicotine content are extracted with cold water. The extract is concentrated, mixed with milk of lime, and steam-distilled. The distillate is acidified with oxalic acid and extracted with ether to dissolve out the hydrocarbon impurities. It is then made alkaline, and the free nicotine extracted with ether.

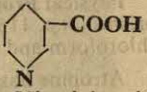
Physical Properties. When freshly prepared, nicotine is a colourless liquid (*b.p.* 246°), readily soluble in water. It has a highly unpleasant, stupefying odour, not unlike that of tobacco. On exposure to air, it rapidly turns brown and resinifies. For this reason, it is possible to distil it unchanged only in *vacuo* or in a current of hydrogen.

Nicotine is a deadly poison, two or three drops, taken internally, are sufficient to cause death in a few minutes. It has one asymmetric carbon atom, and is *levorotatory*. The aqueous solutions of its salts are, however, dextrorotatory.

Chemical Properties and Constitution.

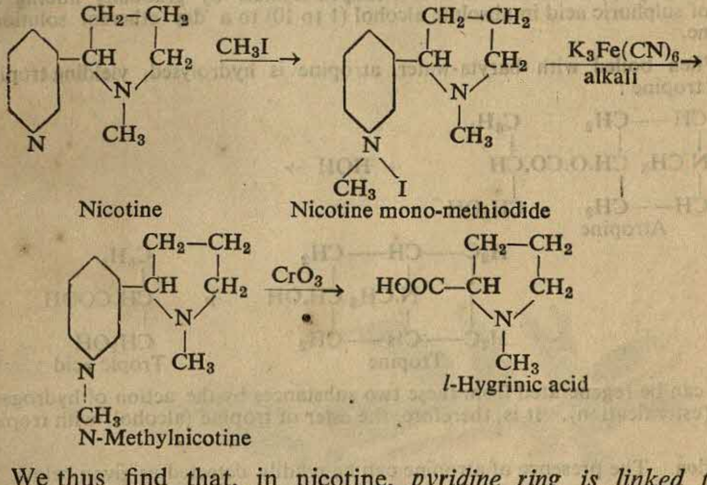
(1) *Properties of a Di-tertiary Base.* As will appear from the formula, nicotine is a *di-tertiary base*. It forms diacid salts, such as the *dihydrochloride*, $C_{10}H_{14}N_2.2HCl$, and combines with two molecules of methyl iodide, yielding the *dimethiodide*, $C_{10}H_{14}N_2.2CH_3I$,

(2) *Oxidation to Nicotinic Acid.* When submitted to oxidation with chromic acid, nicotine yields nicotinic acid (pyridine-β-carboxylic acid). This shows that the nicotine molecule contains a pyridine nucleus substituted in the β-position.



Nicotinic acid

(3) *Conversion into l-Hygrinic acid.* The structure of the other half of the nicotine molecule follows from its conversion into *l*-hygrinic acid :—



Nicotine

Nicotine mono-methiodide

N-Methylnicotine

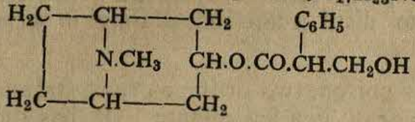
l-Hygrinic acid

We thus find that, in nicotine, *pyridine ring is linked through its β-position to the α-position of N-methylpyrolidine nucleus.*

Detection. Nicotine has no very characteristic reactions. Its presence is readily detected by its odour, which is very characteristic, and recalls the smell of a foul tobacco pipe.

Use. Nicotine is a by-product of the tobacco-growing industry. It is one of the most effective poisons for exterminating greenfly and other insect pests. For this purpose, it is employed in admixture with soft soap and water.

9. Atropine, *tropine ester of di-tropic acid,* $C_{17}H_{23}NO_3$.



Occurrence. Atropine, together with *hyosyamine* and other closely related alkaloids, occurs in the berry of the deadly nightshade (*Atropa belladonna*), in the thorn-apple, the fruits of *datura stramonium*, and in the henbane (*Hyoscyamus niger*). All these plants belong to the Solanum family.

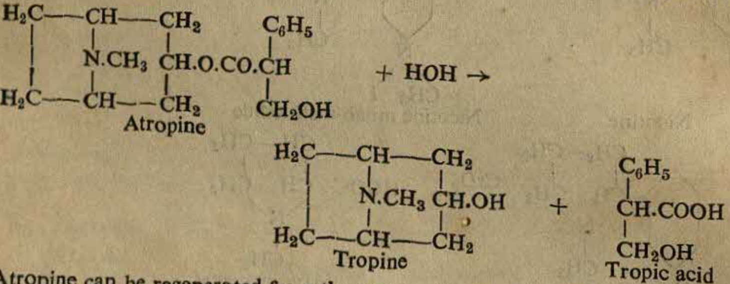
Extraction. Atropine is obtained from the juice of the deadly nightshade. The juice is mixed with potassium carbonate and extracted with chloroform. The chloroform is recovered by evaporation, and the atropine is then extracted from the residue with dilute sulphuric acid. The solution is alkalified with potassium carbonate, when atropine is precipitated. It is purified by recrystallization from alcohol.

Physical Properties. Atropine crystallizes from alcohol and chloroform in prisms (*m.p.* 115°). It is insoluble in water but readily dissolves in alcohol, chloroform and ether.

Atropine has a sharp bitter taste, and is highly poisonous. It has the property of dilating the pupil of the eye, and is therefore extensively used in eye-surgery. It is optically inactive.

Chemical Properties and Constitution. (1) Atropine is a tertiary base and forms well-characterized salts. The **sulphate** $(C_{17}H_{23}NO_3)_2.H_2SO_4.H_2O$, which is used in eye surgery, is obtained as needle-shaped crystals by gradually adding a solution of sulphuric acid in absolute alcohol (1 to 10) to a dry ethereal solution of atropine.

(2) When boiled with baryta-water, atropine is hydrolysed, yielding tropic acid and tropine :



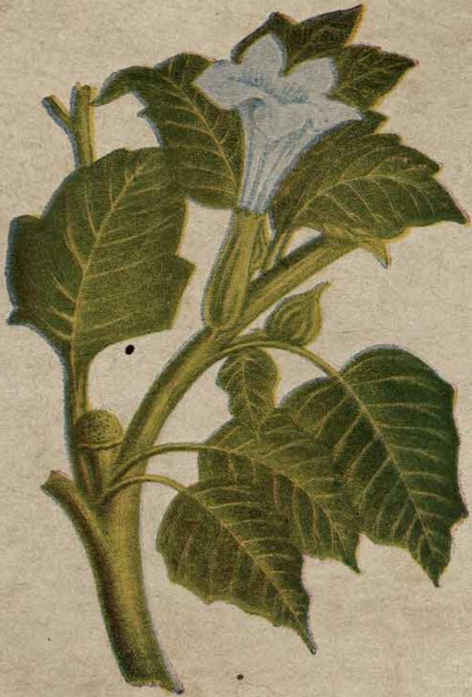
Atropine can be regenerated from these two substances by the action of hydrogen chloride (esterification). It is, therefore, the ester of tropine (alcohol) with tropic acid.

Detection. The presence of atropine can be readily detected as given below.

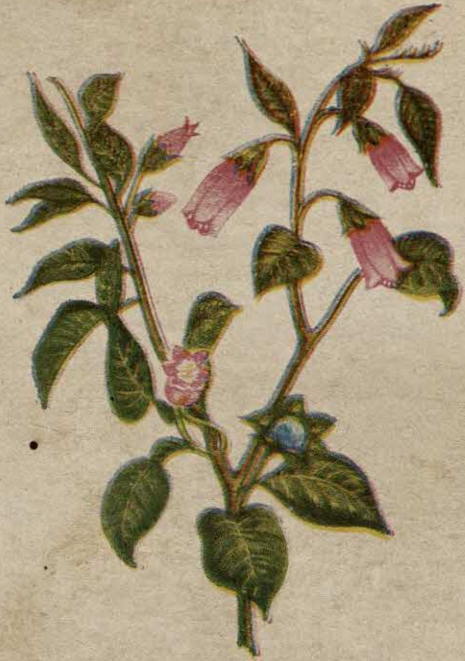
Expt. 1. Moisten a trace of atropine with fuming nitric acid in a small porcelain dish. Evaporate to dryness on a water-bath ; a yellow stain is obtained. Add a few drops of alcoholic potash : an intense violet coloration is developed, which gradually changes to red.

10. Cocaine, $C_{17}H_{21}NO_4$.—Cocaine, together with several other closely related alkaloids, occurs in the leaves of Peruvian coca (*Erythroxylon coca*), from which source it is obtained.

Extraction. The leaves of Peruvian coca are extracted with hot water at about 80°, and the tannins and proteins etc., present in the extract are precipitated by means of lead acetate. The liquid is filtered, lead is precipitated by means of



Datura stramonium



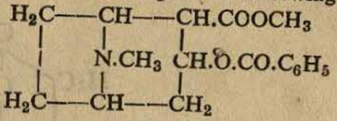
Atropa belladonna

[*To face page 728*]

sodium sulphate and the lead sulphate filtered off. The filtrate is alkalified and the cocaine extracted with ether and purified by crystallization from alcohol.

Cocaine forms colourless crystals, melting at 98°. It is soluble in alcohol and is levorotatory. It is a strong base, and forms salts with acids. The hydrochloride, $C_{17}H_{21}NO_4.HCl$, is readily soluble in water, and is employed in eye surgery and dentistry as a local anaesthetic.

Structural Formula. Cocaine is assigned the following structural formula :



$$\begin{array}{lll} H_2C\text{---} & CH\text{---} & CH.COOCH_3 \\ | & | & | \\ | & N.CH_3 & CH.O.CO.C_6H_5 \\ | & | & | \\ H_2C\text{---} & CH\text{---} & CH_2 \end{array}$$

11. Quinine, $C_{20}H_{24}N_2O_2$.—The bark of different varieties of cinchona, which are grown in India, Ceylon, Bolivia and Peru, contains a number of alkaloids in combination with quinic acid and cinchotannic acid. The two most important alkaloids of the cinchona group are quinine and cinchonine. Quinine is extracted from the cinchona bark as follows :—

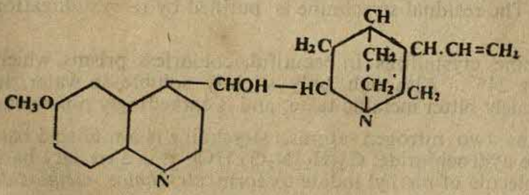
Extraction. The powdered bark is extracted with dilute sulphuric acid, and the resulting solution of the sulphate is treated with caustic soda to precipitate the alkaloids. The mixture of alkaloids thus obtained is dissolved in alcohol, and the solution is neutralized with sulphuric acid. The sulphates, that are thus deposited, are repeatedly crystallized from water. Quinine sulphate, being the least soluble, crystallizes out first, the sulphates of cinchonine and other bases being left behind in the mother-liquor. From the pure sulphate, quinine itself is obtained as an amorphous powder by precipitation with ammonia.

Properties. (1) Quinine crystallizes from water with $3H_2O$. The anhydrous base melts at 173°. It is very sparingly soluble in water, but readily dissolves in alcohol or ether.

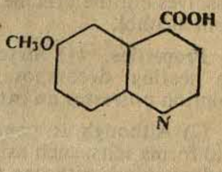
(2) Quinine is a feeble, di-acid base, and forms well-defined salts with acids, of which the sulphate ($C_{20}H_{24}N_2O_2.H_2SO_4.8H_2O$), and the hydrochloride ($C_{20}H_{24}N_2O_2.2HCl.2H_2O$) are most commonly employed.

(3) Quinine is a di-tertiary base and combines with methyl iodide to give a dimethiodide, $C_{20}H_{24}N_2O_2, (CH_3I)_2$.

(4) When subjected to oxidation by means of chromic acid, quinine yields **quininic acid** (*p*-methoxyquinoline-γ-carboxylic acid). Quinine is therefore a derivative of quinoline, and has the structure given below :



Quinine



Quininic acid

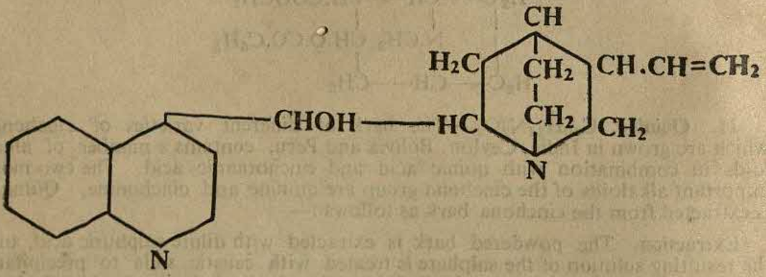
Tests. (1) Dilute solutions of quinine salts exhibit a splendid blue fluorescence.

When a solution of a quinine salt is treated with chlorine or bromine water, followed by ammonia, a green precipitate is obtained. This dissolves in excess of ammonia, yielding an emerald-green solution.

Use. Quinine is much used as a specific against malaria. It also acts as an antidote against many infections caused by micro-organisms.

12. Cinchonine, $C_{19}H_{22}N_2O$.—As already stated, cinchonine occurs, together with quinine, in the cinchona bark. It is obtained from the mother liquor from which quinine sulphate has been crystallized out (see under quinine).

The mother liquor is alkalified with sodium hydroxide, when cinchonine gets precipitated. The precipitate is dissolved in the smallest possible quantity of boiling alcohol. The solution, on cooling, deposits cinchonine, which is purified by the crystallization of its sulphate from water.



Cinchonine

Cinchonine forms colourless prisms, which melt at 225°. It resembles quinine in its general behaviour, and is a di-tertiary base. Like quinine, it acts as an antipyretic, though it is much less active.

Structure. Cinchonine has been given a structure analogous to that of quinine, which, in fact, is a *methoxy*-cinchonine.

13. Strychnine, $C_{21}H_{22}N_2O_2$.—The two highly poisonous alkaloids, strychnine and brucine are contained in the seeds of *strychnos nux vomica* and *strychnos ignatii* (Ignatus beans). They are usually obtained from the former.

Extraction. The powdered seed of nux vomica is extracted with boiling dilute alcohol; the solution is evaporated, to boil off the alcohol, and the residual aqueous solution is treated with lead acetate to precipitate tannin, proteins, etc. The filtrate is treated with hydrogen sulphide to precipitate the lead, and the liquid is filtered and then boiled, to remove respectively the lead sulphide and the excess of hydrogen sulphide. The solution is treated with magnesia to precipitate the alkaloids, and the precipitate, after being allowed to stand, is filtered. The mixture of the two alkaloids thus obtained is treated with a little alcohol, which dissolves out the brucine. The residual strychnine is purified by recrystallization from alcohol.

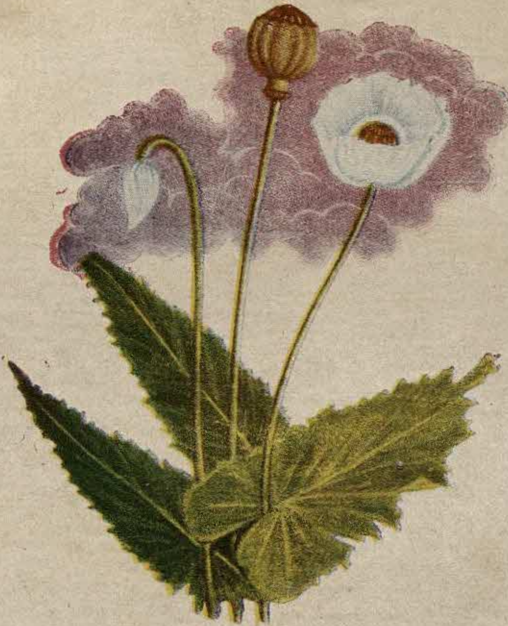
Properties. (1) Strychnine crystallizes in beautiful, colourless prisms, which, on heating, decompose at 245°. Although only slightly soluble in water, its solution possesses an extremely bitter metallic taste, and is exceedingly poisonous.

(2) Although it contains two nitrogen atoms, strychnine is a monacid base and forms salts, such as the hydrochloride, $C_{21}H_{22}N_2O_2.HCl$. It is a tertiary base, and combines with one molecule of methyl iodide to form *strychnine methiodide*, $C_{21}H_{22}N_2O_2,CH_3I$.

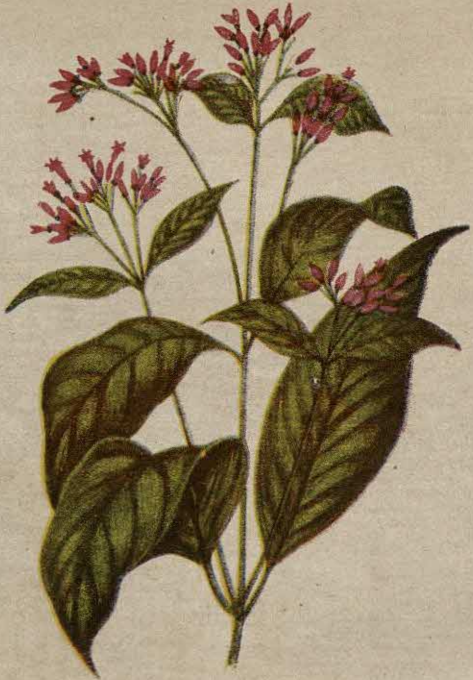
(3) When distilled with alkali, it yields, among other products, quinoline. Hence the molecule must contain a quinoline ring.

Test. A small quantity of strychnine salt is treated with a little concentrated sulphuric acid in a porcelain dish, and then a little powdered potassium dichromate is added. An intense violet solution is produced, which gradually turns bright red and then yellow.

Use. In minute doses strychnine is used in medicine. It is also employed as a poison for dogs, rabbits and mice.



Papaver somniferum



Cinchona officinalis
[*To face page 731*]

14. Brucine, $C_{23}H_{26}N_2O_4$.—Brucine occurs together with strychnine in the seeds of *nux vomica.*

Extraction. The alcoholic solution of brucine, obtained as described under strychnine, is evaporated to dryness. The residue, which still contains strychnine, is dissolved in acetic acid. The solution is evaporated, when strychnine separates out[1]. The stable brucine acetate is dissolved in water, and the strychnine is filtered off. The filtrate is then treated with sodium hydroxide to precipitate brucine, which is purified by crystallization from dilute alcohol.

Properties. Brucine crystallizes from hot water in colourless prisms containing $4H_2O$. When anhydrous, it melts at 78°. It is slightly soluble in water and alcohol, though more so than strychnine, but is much less active. Like strychnine brucine is a monacid base.

Test. When a trace of a brucine salt is treated with nitric acid, a deep brown-red coloration is developed, which changes to yellow on warming; if stannous chloride is now added, intense violet coloration is obtained.

Conversely, the test may be utilized for the detection of even minute quantities of nitric acid or the nitrates.

15. Morphine, $C_{17}H_{19}NO_3$.—Opium, the dried juice of the seed-capsules of poppy (*Papaver somniferum*), is a very complex mixture, containing among other substances, caoutchouc, fats, resins, carbohydrates, proteins, mineral salts, meconic acid, and about twenty or more alkaloids. Of these alkaloids, morphine is the most important, and constitutes about 10 per cent of opium.

Extraction. Opium is extracted with boiling water, and the solution, which contains the salts of the bases is rendered alkaline with milk of lime. Calcium meconate and the other alkaloids are precipitated while the morphine remains in solution. The filtrate is concentrated and warmed with ammonium chloride, until no more ammonia is evolved. This converts the lime present in the solution into calcium chloride. The solution is then allowed to stand for some days, when morphine separates out, and is purified by crystallization from boiling alcohol.

Properties. (1) Morphine crystallizes from aqueous alcohol in colourless prisms, containing $1H_2O$. It possesses a bitter taste, and is only sparingly soluble in water and alcohol.

(2) Morphine readily dissolves in alkalis, from which it may be reprecipitated by the addition of acids.

(3) Morphine acts as a monacid base, and combines with acids, yielding well-defined salts. The hydrochloride, $C_{17}H_{19}NO_3.HCl$, crystallized from water with $3H_2O$, and is the salt commonly employed in medicine.

(4) It is a tertiary base, and combines directly with one molecule of methyl iodide, yielding *morphine methiodide*, $C_{17}H_{19}NO_3.CH_3I$.

(5) When distilled with zinc-dust, morphine yields, among other substances, a considerable quantity of phenanthrene.

Tests. (1) Ferric chloride, when added to a solution of morphine or a morphine salt, yields a deep blue coloration.

(2) If a few drops of a solution of morphine hydrochloride are added to a small quantity of an aqueous solution of iodic acid, iodine is set free, and may be detected by its brown colour and by the production of the characteristic deep blue coloration with starch.

(3) A most delicate test for morphine is as under : The alkaloid is dissolved in concentrated sulphuric acid, and the solution is allowed to stand for 15 hours. At the end of this time, some concentrated nitric acid is added when a deep bluish violet colour is developed, which gradually changes to blood-red.

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[1] This is due to the instability of strychnine acetate; the acetic acid evaporates off, while strychnine separates out.

Use. Morphine hydrochloride is used in medicine as a soporific and for the alleviation of pain.

QUESTIONS

1. What are the general methods by which alkaloids are isolated from plants? What are the general methods employed in determining the constitution of alkaloids? Give suitable examples. *(Bombay, B.Sc., 1944)*

2. Describe a method for the quantitative estimation of methoxy (—OCH_3) group in an organic compound.

When treated according to Zeisel's method, 0·226 gm. of an alkaloid, $C_{20}H_{21}O_4N$, yields 0·626 gm. of silver iodide. Calculate the number of methoxy groups present in the molecule of the alkaloid. *(Punjab, B.Sc., 1936)*

3. Discuss the structure of piperine. *(Madras, B.Sc., 1955)*

4. Describe the preparation, synthesis and properties of coniine. Establish the constitution. *(Lahore, B.Sc., 1956)*

5. What are alkaloids? Discuss the constitution of nicotine. Give its synthesis. *(Poona, B.Sc., 1957)*

6. How is nicotine obtained from tobacco leaves? Suggest a method for its synthesis. *(Andhra, B.Sc., 1953)*

7. You are given a quantity of cinchona bark, describe the method that you would adopt to extract a pure sample of quinine from it. Give the most important properties of this alkaloid, and also describe a method by which the presence of quinine could be detected in a given solution.

8. What do you understand by the term alkaloid? Give an account of the evidence available in favour of the structure assigned to Coniine or Nicotine. *(Karachi, B.Sc., 1957)*

9. Discuss the constitution of coniine and give its synthesis. *(Poona, B.Sc., 1958)*

10. How would you show that nicotine contains a pyrrolidine nucleus? Describe the synthesis of nicotine. *(Andhra, B.Sc., 1958)*

11. What are alkaloids? How are they obtained from their vegetable sources? Write constitutional formulae for piperine and coniine. *(Rajasthan, B.Sc., 1958)*

12. Describe the chemistry of nicotine and its synthesis. Mention the tests used for the detection of alkaloids. *(Bombay, B.Sc., 1955)*

13. Discuss the constitution of Atropine and give its synthesis *(Gujarat, B Sc , 1955)*

14. Discuss the constitution of Cocaine and give its synthesis. *(Gujarat, B.Sc., 1959)*

15. Establish the structure of coniine. *(Madras, B.Sc., 1960)*

16. What do you understand by the term alkaloids? Describe the constitution of coniine. *(Ajmer, B.Sc., 1961)*

17. Discuss the analytical and synthetic evidence on which the structure of piperine is based. *(Venkateswara, B.Sc., 1961)*

18. What do you understand by the term alkaloids? Describe the constitutions of coniine. *(Rajasthan, B.Sc., 1961)*

CHAPTER FIFTY-SEVEN

TERPENES

1. Occurrence.—The **terpene hydrocarbons**, $C_{10}H_{16}$, and their oxygenated derivatives, called **camphors**, ($C_{10}H_{16}O$, $C_{10}H_{18}O$, etc.) form the most important constituents of **essential oils** occurring in flowers, leaves and roots of many kinds of plants. They are also found in wood, *e.g.*, in the resin sap of pine, in sandal wood and in camphor wood. Essential oils are recovered from the vegetable material by steam-distillation or by extraction with solvents. They are usually mixtures of various liquids, but in certain cases, *e.g.*, camphor, they may be solids also.

2. Structure and Classification.—The fundamental unit of which the terpene and camphor molecules are built up is the dialkene **isoprene**[1] (*2-methyl-1,3-butadiene*), $H_2C{=}C(CH_3){-}CH{=}CH_2$. These compounds, therefore, are often referred to as **isoprenoid compounds**-Many terpenes are unsaturated in character, and give crystalline additive compounds with NOCl, Br_2, HBr, HCl, N_2O_3 and NO_2. These addition compounds serve to isolate unsaturated terpenes from their naturally occurring mixtures. The terpenes can, in most cases, be recovered in a pure state from the addition compounds.

Terpenes are classified on the basis of isoprene units that the molecule is built from. Thus, we have *hemiterpenes*, C_5H_8, *monoterpenes*, $C_{10}H_{16}$, *sesquiterpenes*, $C_{15}H_{24}$, *diterpenes*, $C_{20}H_{32}$, *triterpenes*, $C_{30}H_{48}$, and *polyterpenes*, $(C_5H_8)_n$.

From the view-point of molecular structure, simple terpenes are divided into **three classes :** (*i*) Acylic terpenes, (*ii*) Monocyclie terpenes and (*iii*) Bicyclic terpenes.

ACYCLIC MONOTERPENES

3. Myrcene. $C_{10}H_{16}$.—This is an acyclic monoterpene hydrocarbon. It occurs in oils of bay, verbena and hops, but is industrially unimportant.

Myrcene is a liquid that boils at 166—168°.

Constitution. The constitution of myrcene follows from the following considerations :

1. Catalytic Hydrogenation[2] of myrcene, $C_{10}H_{16}$, ultimately yields a decane,

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[1] Refer to sec. 13, page 166.

[2] *i.e* hydrogenation in the presence of platinum as catalyst.

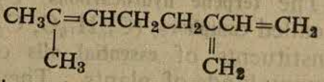
When treated with sodium and alcohol, myrcene gives a dihydro-derivative, two hydrogen atoms being added to the conjugated system.

$C_{10}H_{22}$, showing that it is an open-chain hydrocarbon containing three double bonds in the molecule.

2. With maleic anhydride, it forms an "adduct" (*i.e.* a six-membered ring, formed as the result of addition taking place at the 1, 4-positions). Hence, two out of the three double bonds are conjugated.

3. Ozonolysis of the hydrocarbon yields acetone, formaldehyde and a keto-dialdehyde, which, on oxidation, gives succinic acid and carbon dioxide.

The above facts establish the constitution of myrcene as **7-methyl-3-methylene-1,6-octadiene :**



$$CH_3\underset{\overset{|}{CH_3}}{C}=CHCH_2CH_2\underset{\overset{\|}{CH_2}}{C}CH=CH_2$$

The presence of a conjugated system of double bonds in the myrcene molecule is fully supported by the ultra-violet absorption spectrum of the hydrocarbon.

Another important evidence in support of the above formula of myrcene is that, in the presence of dilute sulphuric acid, it gets hydrated to an alcohol, which, when oxidized, yields citral. . The constitution of this last named compound has been established on independent evidence (p. 735 , and the conversion of myrcene to citral is in full agreement with the above structure of the hydrocarbon.

Indentification.—

Myrcene may be identified by the following physical constants :

(1) Its boiling-point : 166—168°.
(2) Maleic anhydride adduct melts at 34—35°.
(3) 1, 4-Naphthoquinone adduct melts at 80—81°.

4. Ocimene, $C_{10}H_{16}$.—This is another naturally-occurring acyclic monoterpene hydrocarbon. It occurs in the oil of *Ocimum basilicum*, but has not found any commercial application so far.

Ocimene is a liquid boiling at 176—178°.

Ocimene has been shown to be a mixture of the following two forms, in which (1) predominates.

(1) $CH_2=C(CH_3)CH_2CH_2CH=C(CH_3)CH=CH_2$
3, 7-Dimethyl-1,3,7-octatriene

(2) $(CH_3)_2C=CHCH_2CH=C(CH_3)CH=CH_2$
3, 7-Dimethyl-1, 3, 6-octatriene

5. Citral, $C_{10}H_{16}O$.—Citral, also called **Geranial**, is the pivotal member of the acyclic monoterpenes, as the structures of most of the other compounds of this category are based on that of citral.

Citral occurs in many essential oils, particularly in verbena oil, lemongrass oil and in lemon oil. It is obtained commercially from lemongrass oil, in which it occurs to the extent of 70 to 90 per cent.

Citral is a yellowish oil with a strong, pleasant odour of lemons. It boils at 228°.

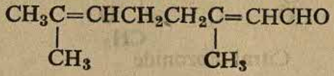
Uses.—(1) Citral is used as a perfume.

(2) It is the starting material for the manufacture of ionones and methylionones that form the basis of artificial violet scents.

(3) Citral is also the starting material for the synthesis of vitamin A.

Constitution of Citral.—

Citral has been shown to be **3,7-dimethyl-2,6-octadienal :**

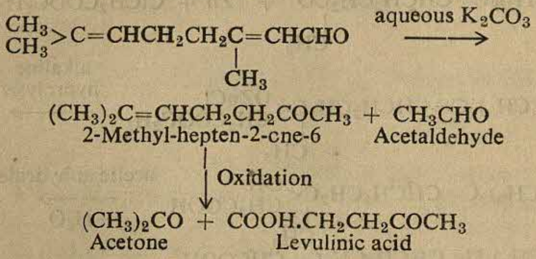


$$CH_3\underset{|\atop CH_3}{C}{=}CHCH_2CH_2\underset{|\atop CH_3}{C}{=}CHCHO$$

This conclusion is based on the following three facts, and has been verified by synthesis. The basic facts are :—

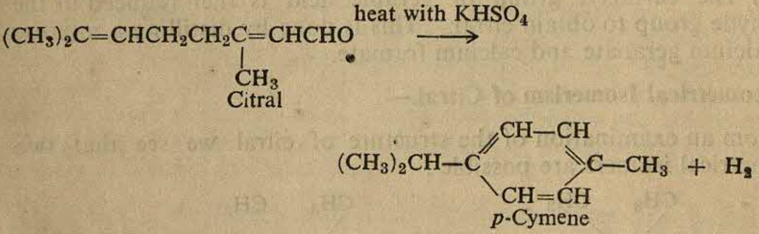
(1) Citral gives typical reactions of an aldehyde, and forms a bisulphite compound and an oxime.

(2) When heated with an aqueous solution of potassium carbonate, it undergoes scission[1] to give acetaldehyde and methylheptenone[2]. The constitution of the latter compound follows from the fact that, when submitted to oxidation, it gives acetone and levulinic acid :—



$$\begin{array}{c} {CH_3 \atop CH_3}\!>\!C{=}CHCH_2CH_2\underset{|\atop CH_3}{C}{=}CHCHO \xrightarrow{\text{aqueous } K_2CO_3} \\ \underset{\text{2-Methyl-hepten-2-cne-6}}{(CH_3)_2C{=}CHCH_2CH_2COCH_3} + \underset{\text{Acetaldehyde}}{CH_3CHO} \\ \Big\downarrow \text{Oxidation} \\ \underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Levulinic acid}}{COOH.CH_2CH_2COCH_3} \end{array}$$

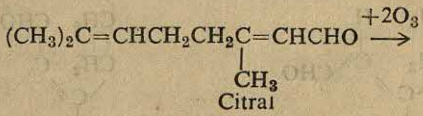
(3) When heated with potassium hydrogen sulphate, citral cyclizes to *p*-cymene, a reaction that shows the relative positions of the methyl and isopropyl groups in the citral molecule :



$$\underset{\text{Citral}}{(CH_3)_2C{=}CHCH_2CH_2\underset{|\atop CH_3}{C}{=}CHCHO} \xrightarrow{\text{heat with } KHSO_4}$$

p-Cymene

(4) Ozonolysis of citral gives acetone, levulinic aldehyde and glyoxal, which clearly indicates the positions of the two double bonds :

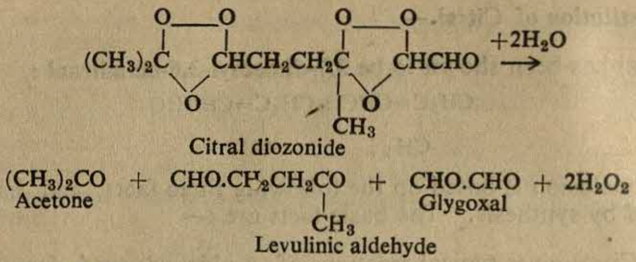


$$\underset{\text{Citral}}{(CH_3)_2C{=}CHCH_2CH_2\underset{|\atop CH_3}{C}{=}CHCHO} \xrightarrow{+2O_3}$$

---

[1] This is a reversal of aldol condensation (p. 278).

[2] Systematic name : 2-Methyl-hepten-(2)-one (6).



$$(CH_3)_2C(O_3)CHCH_2CH_2C(CH_3)(O_3)CHCHO \xrightarrow{+2H_2O} (CH_3)_2CO + CHO.CH_2CH_2CO(CH_3) + CHO.CHO + 2H_2O_2$$

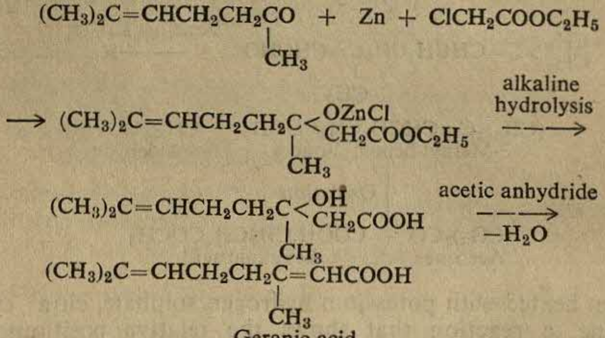
Citral diozonide

Acetone Levulinic aldehyde Glygoxal

Synthesis of Citral.—

Citral has been synthesized from synthetic methylheptenone in two steps :

(1) Conversion of methylheptenone into geranic acid by Reformatsky reaction, using zinc and ethyl chloroacetate :



$$(CH_3)_2C{=}CHCH_2CH_2CO(CH_3) + Zn + ClCH_2COOC_2H_5$$

$$\longrightarrow (CH_3)_2C{=}CHCH_2CH_2C(CH_3){<}^{OZnCl}_{CH_2COOC_2H_5} \xrightarrow{\text{alkaline hydrolysis}}$$

$$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){<}^{OH}_{CH_2COOH} \xrightarrow[-H_2O]{\text{acetic anhydride}}$$

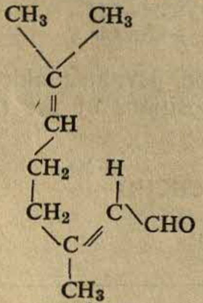
$$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCOOH$$

Geranic acid

(2) The carboxyl group of geranic acid is then reduced to the aldehyde group to obtain citral. This is done by distilling a mixture of calcium geranate and calcium formate.

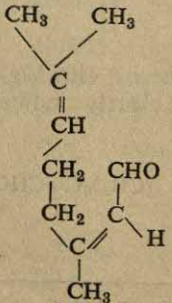
Geometrical Isomerism of Citral.—

From an examination of the structure of citral we see that two geometrical isomers are possible :



trans-form
Citral-*a*

and



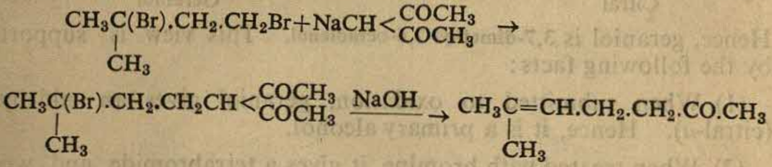
cis-form
Citral-*b*

Both the *trans* and the *cis* forms occur in naturul citral, which, when treated with semicarbazide, gives two semicarbazones. The *trans*-form of citral, called **citral-*a*** or **geranial** boils at 118-119° under 20 mm. pressure, while the *cis*-form, called **citral-*b*** or **neral** boils at 117-118° under 20 mm. pressure.

The configurations of the two forms of citral have been determined by reference to the readiness with which the ring closure of the corresponding stereoismeric primary alcohols, namely geraniol and nerol, occurs (p. 738).

Synthesis of Methylheptenone.[1]—

The synthesis of this compound, leading to the establishment of its structure as 2-methyl-2-hepten-6-one, was first carried out by Barbier and Bouveault in 1896. It consists in condensing 2,4-dibromo-2-methylbutane with sodio-acetylacetone and heating the product with a concentrated solution of NaOH :—



$$CH_3\underset{CH_3}{C}(Br).CH_2.CH_2Br + NaCH<\begin{matrix}COCH_3\\COCH_3\end{matrix} \rightarrow$$

$$CH_3\underset{CH_3}{C}(Br).CH_2.CH_2CH<\begin{matrix}COCH_3\\COCH_3\end{matrix} \xrightarrow{NaOH} CH_3\underset{CH_3}{C}=CH.CH_2.CH_2.CO.CH_3$$

6. Geraniol, $C_{10}H_{18}O$.—This terpene alcohol occurs in a large number of essential oils, notably the rose, palmarosa, citronella, geranium, coriander and neroli. The **rose oil**, obtained by steam distillation of fresh flowers of *Rosa damascena*, contains 40 to 60 per cent of geraniol, which, however, is not extracted from this source because of high cost of rose oil. This oil is used primarily for high-grade perfumery.

The best grade of geraniol is obtained from **palmarosa oil** (got by steam distillation of the wild-growing grass *Cymbopogon martini* found in East Indies), which contains as much as 84—94 per cent of geraniol. Another important source of commercially valuable but inferior grade of geraniol is the Java-type **citronella oil**, obtained by steam distillation from the grass *Cymbopogon winterianus*, cultivated in Java, Formosa and elsewhere.

Isolation. Geraniol is readily obtained pure from the palmarosa or citronella oil by making use of its property to form an addition compound with calcium chloride, which is separated and subsequently decomposed. Another, though less satisfactory, method consists in crystallization of its acid phthalate.

Uses. (1) The most important use of geraniol is in perfumery, particularly as a component of artificial rose scents.

(2) It finds some use as a soap perfume.

---

[1] **Methylheptenone,** though not itself a terpenoid, is connected in many ways with the chemistry of terpenes. It is a liquid with a floral odour and boils at 170-171°.

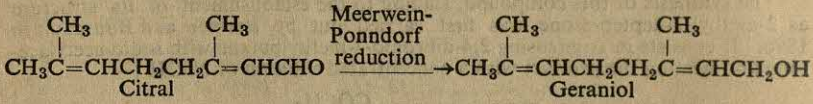
(3) Its esters, too, find frequent use in perfumery. Geraniol acetate, formate and butyrate are employed in rose, lavender, geranium, jasmine and neroli preparations.

(4) Geraniol is also employed in the preparation of flavour compounds, particularly apple, apricot and pear.

(5) An interesting use of geraniol is in insect baits.

Constitution of Geraniol.—

The constitution of geraniol follows directly from its relationship with citral, which, when submitted to Meerwein-Ponndorf reduction[1] (p. 228), yields geraniol :



$$\underset{\text{Citral}}{CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}=CHCHO} \xrightarrow{\substack{\text{Meerwein-}\\ \text{Ponndorf}\\ \text{reduction}}} \underset{\text{Geraniol}}{CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}=CHCH_2OH}$$

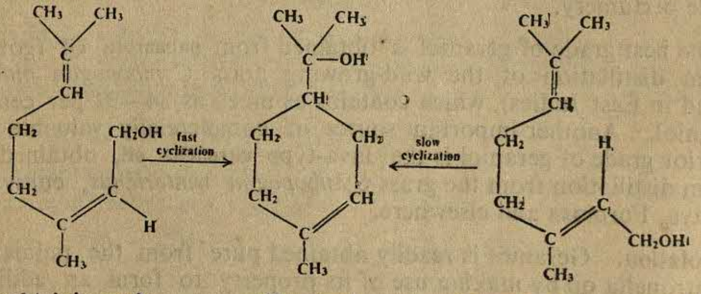
Hence, geraniol is **3,7-dimethyl-2,6-octadienol.** This view is supported by the following facts:

(1) When submitted to oxidation, geraniol gives an aldehyde (citral-*a*). Hence, it is a primary alcohol.

(2) When treated with bromine, it gives a tetrabromide, and when submitted to catalytic hydrogenation it adds on four hydrogen atoms, proving the presence of two double bonds in the molecule.

Geometrical Isomerism of Geraniol and Nerol.[2]

Reduction of citral produces mainly geraniol, but a small quantity of nerol is produced at the same time. Nerol has been shown to be structurally identical with geraniol ; both possess the same chemical properties. They are, in fact, geometrical isomers. Nerol, however,



Nerol (*cis*-isomer) α-Terpineol Geraniol (*trans*-isomer) undergoes cyclization to α-terpinol about nine times as fast as geraniol. Hence, nerol is given the *cis*- and geraniol the *trans*-configuration.

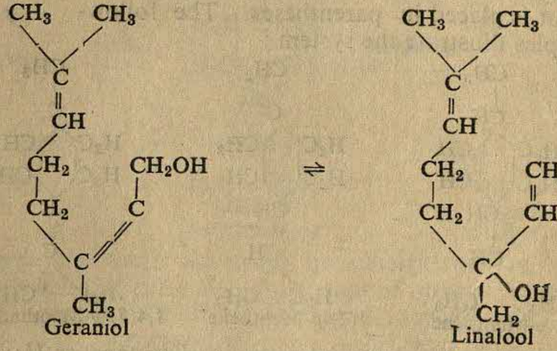
---

[1] An alternative method of bringing about this selective reduction is by the use of platinum, as the catalyst, in the presence of a trace of ferrous salt and a trace of zinc acetate. The ferrous salt serves to promote reduction of the carbonyl group and the zinc salt inhibits reduction taking place at the double bonds.

[2] Nerol, like geraniol, occurs naturally in certain essential oils, particularly of neroli and bergamot. It is structurally identical with and is the *cis*-form of geraniol. It boils at 225-226°C.

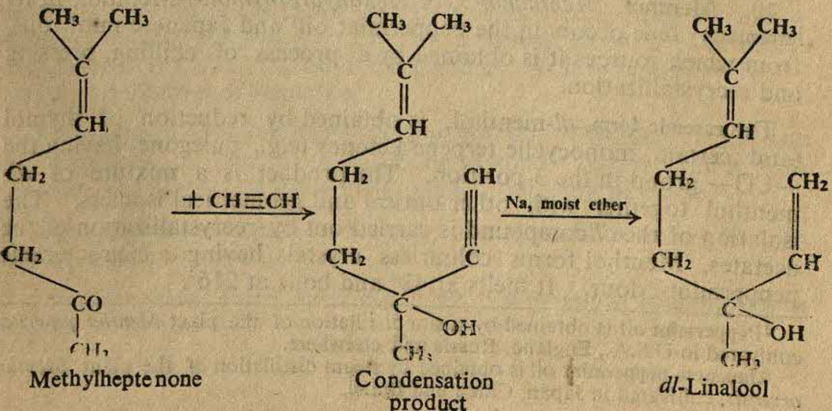
7. **Linalool**, $C_{10}H_{18}O$.—Linalool or **linalyl alcohol**, is a tertiary alcohol and exists in nature both in the *d*- and the *l*- forms. *d*-Linalool occurs in the oils of rosewood, coriander and linaloe-seed. The *l*-form is found in the oils of bergamot, lavender and linaloe-wood. Both the forms boil at 198-199°C.

The racemic or inactive form of linalool does not occur in nature, but is obtained by the isomerization of geraniol, which occurs in the presence of acids. Since the structure of geraniol is known, a possible structure for linalool may be deduced on the basis of allylic rearrangement :



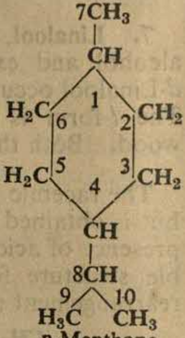
Synthesis of Linalool.—

The above structural formula of linalool has been confirmed by Ruzicka (1919) by synthesizing the compound from methylheptenone as follows :



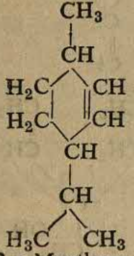
MONOCYCLIC MONOTERPENES

8. General.—The nomenclature of monocyclic monoterpenes is based on the fully saturated hydrocarbon, **hexahydro-*p*-cymene** or ***p*-menthane.** The structure of menthane and the numbering of its carbon atoms is shown in the margin for reference.

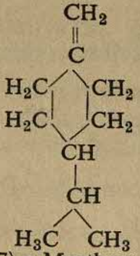


p-Menthane

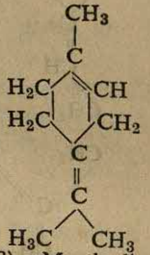
Unsaturated hydrocarbons derived from methane are termed ***p*-menthenes,** when there is one double bond in the molecule, and **menthadienes,** when there are two double bonds. The position of the double bond is indicated, as usual, by the *first* carbon atom carrying the double bond. In case, however, there is any ambiguity the *second* carbon atom of the double bond is also mentioned, but is placed in parentheses. The following examples illustrate the system :



2-*p*-Menthene



1(7)-*p*-Menthene



1,4(8)-*p*-Menthadiene

9. *p*-Menthane, *1-Isopropyl-4-methylcyclohexane*, or *Hexahydrocyme*, $C_{10}H_{20}$.—This is the parent hydrocarbon from which cyclic monoterpenes may be regarded as derived. It does not occur in nature, but can be readily obtained by the hydrogenation of *p*-cymene or of any of the monocyclic terpenes.

p-Menthane is a colourless liquid boiling at 170·7°C.

10. Menthol, *Menthanol-3*, or *Hexahydrothymol*.—Menthol, in its **levorotatory form** occurs in the peppermint oil[1] and Japanese mint oil[2], from which sources it is obtained by a process of chilling, pressing and recrystallization.

The **racemic form,** *dl*-menthol, is obtained by reduction of thymol (and certain monocyclic terpene ketones (*e.g.*, pulegone) having the —CO— group in the 3-position. The product is a mixture of *dl*-menthol together with other optical and geometrical isomers. The isolation of the *dl*-compound is carried out by recrystallization of the acetates. Menthol forms colourless crystals having a characteristic peppermint-odour. It melts at 43° and boils at 216°.

---

[1] Peppermint oil is obtained by steam distillation of the plant *Mentha piperita*, cultivated in U.S.A., England, Russia and elsewhere.

[2] Japanese peppermint oil is obtained by steam distillation of the plant *Mentha arvensis*, cultivated in Japan, China and Brazil.

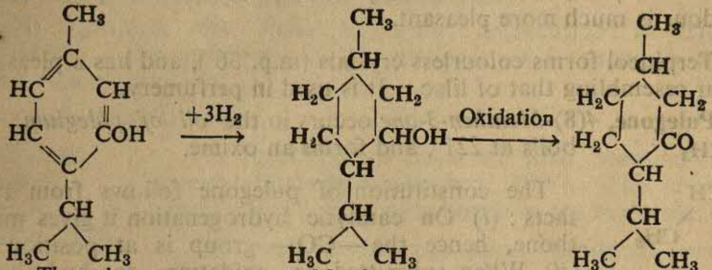
Uses of Menthol.—(1) Menthol, natural as well as synthetic, possesses mild antiseptic properties, and is employed in toothpastes, nasal sprays, gargles, toilet creams and cleansing lotions.

(2) Large quantities of menthol are used by the pharmaceutical and flavour industries.

(3) It also finds a limited application in perfumery.

Constitution of Menthol.—

The constitution of menthol follows from that of thymol (p. 641) from which, as already stated, it may be obtained by hydrogenation. When submitted to oxidation, it gives a ketone, $C_{10}H_{18}O$, called **menthanone** or **menthone**. Hence, menthol is a secondary alcohol. The following scheme shows the structural relationship of the three compounds :—



Thymol

Menthol (menthanol-3)

Menthone (menthanone-3)

Stereoisomers. As there are three asymmetric carbon atoms in menthol, eight stereoisomers (*i.e.*, four pairs of optical antipodes) are theoretically possible. Of these, five are known (*d*- and *l*-menthol, m.p. 43°, *d*- and *l*-neomenthol, m.p. −22°, and *d*-neoisomenthol, m p. −8°). In menthol, the methyl and isopropyl groups are in the *trans*-position; the hydroxyl group is in the *cis*-position with respect to the methyl group. In neomenthol, the methyl and isopropyl groups are in the *trans*-position, as in the case of menthol, but the hydroxyl is in the *cis*-position with respect to the isopropyl group.

11. Menthone, $C_{10}H_{18}O$, *Menthan-3-one*, occurs both in the *d*- and the *l*-form in essential oils. The *d*- form is present in oil of pennyroyal (*Mentha pulegium*), of which it forms 90 per cent or more. *l*-Menthone occurs in the oil of peppermint. It is prepared synthetically by oxidation of *l*-menthol.

Menthone is a colourless liquid (*b.p.* 208°C). Chemical behaviour of menthone is that of a saturated ketone. On reduction with sodium and alcohol, it gives the secondary alcohol, *menthol*.

The structure of menthone follows from that of menthol, which, as we have seen, is methan-3-ol.

Menthone finds some use in medicine, but mainly it is employed as a soap perfume.

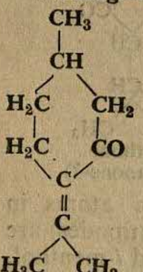
12. Menthenes and Their Derivatives.—The unsaturated hydrocarbons derived from menthane containing only *one* double bond are called *menthenes.* All the six possible menthenes (*viz.* 1-, 2-, 3-, 1(7), 4(8) and 8-menthene) are known, but are of little importance.

α-Terpineol, *1-Menthen-8-ol,* occurs in certain essential oils, notably cajeput oil, neroli oil and pine oil. It is from the last source that commercial α-terpineol (which is about 90 per cent pure) is obtained.

Another important commercial source is *terpin* (1,8-menthanediol), which is obtained by the hydration of α-pinene of turpentine oil. Terpin, when heated with phosphoric acid or oxalic acid, loses a molecule of water, yielding a mixture of α-, β- and γ-terpineols[1] in which the α-compound predominates. The mixture is known in trade as **terpineol extra,** and is considered superior to the natural product, as its odour is much more pleasant.

α-Terpineol forms colourless crystals (m.p. 36°), and has a pleasant odour resembling that of lilac. It is used in perfumery.

d-**Pulegone,** *4*(8)-*Menthen-3-one* occurs in the *oil of pulegium.* It boils at 221°, and forms an oxime.



Pulegone

The constitution of pulegone follows from two facts : (*i*) On catalytic hydrogenation it gives menthone, hence the —CO— group is at position 3. (*ii*) When submitted to oxidation or hydrolysis, pulegone *yields* acetone ; hence the position of the double bond must be between carbon atoms 4 and 8.

13. Menthadienes and their Derivatives.—The unsaturated hydrocarbons derived from menthane and containing *two* double bonds are called menthadienes. Their general molecular formula is $C_{10}H_{16}$. Many menthadienes occur in nature as constituents of essential oils.

Limonene, $C_{10}H_{16}$, *1,8(9)-Menthadiene,* occurs in nature in *d*-, *l*- and racemic forms. *d*-Limonene is the chief constituent of oils of lemon, bitter orange and caraway. The *d*-form occurs in pine-needle oil. The racemic form, known as **Dipentene,** is found in considerable quantities in the oil of turpentine

Manufacture of Limonene and Dipentene. Limonene is commercially obtained from the following sources :—

(1) *From Orange Oil. d*-Limonene is obtained from orange oil, of which increasing quantities are becoming available from the frozen or canned juice industry.

(2) *From Turpentine Oil.* The oil obtained from 'colophony' by steam distillation is a valuable source of terpenes. It is submitted to

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[1] β- and γ- Terpinols are 8-menthene-1-ol and 4(8)-menthene-1-ol respectively. The β-compound melts at 33° and the γ- at 68°C.

fractional distillation to give extracting solvent, bicyclic terpene and monocyclic terpene fractions. The last named, on refractionation, gives dipentene and terpinolene.

(3) Some dipentene is also obtained as a by-product in certain acid-catalysed reactions of α-pinene, such as isomerization to camphene and hydration to pine oil.

Uses :

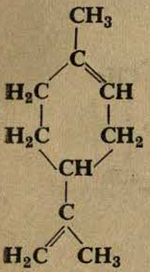
(1) *Orange Oil*, consisting principally of *d*-limonene, is used as a flavour in beverages, pharmaceutical preparations and foods.

(2) "*Terebene*", consisting chiefly of dipentene and terpinenes, is used in medicine as an expectorant.

(3) Dipentene is employed in making sulphurized high-pressure lubricating-oil additives and synthetic resins.

(4) Dipentene also finds important application in chemical industries. It is employed in the synthesis of isoprene, *p*-cymene and *p*-menthane.

Constitution of Limonene.—



(1) Treatment of limonene with bromine yields a crystalline **tetrabromide** (*m.p.* 105°). This shows the presence of two double bonds in the molecule.

(2) Catalytic hydrogenation produces **menthane**, which shows the structure of the carbon framework.

(3) The positions of the two double bonds follow from the fact that limonene is produced from α-terpineol (1-menthen-8-ol), when the latter is heated with $KHSO_4$ Loss of a molecule of water occurs and a second double bond comes into existence between the carbon atoms 8 and 9.

BICYCLIC MONOTERPENES

14. General.—The molecule of a bicyclic monoterpene consists of *two* rings, one of which is 6-membered ; other one may be 3-, 4- or 5- membered.[1] The naturally occurring bicyclic terpenes are chiefly derived from the parent hydrocarbons, thujane, carane pinane and camphane, which are all saturated and possess the molecular formula, $C_{10}H_{18}$ (as compared, to $C_{10}H_{20}$ of menthane). The structural formulae of these are given on the next page.

15. **α-Pinene, $C_{10}H_{16}$.**—The two unsaturated hydrocarbons derived from pinane[2], called α-pinene and β-pinene, are the chief constituents of the turpentine oil[3]; the α-compound greatly predominates. The

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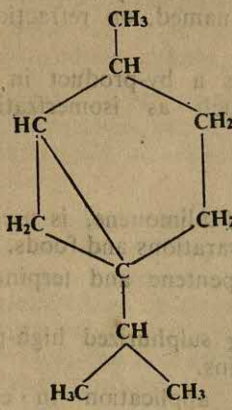
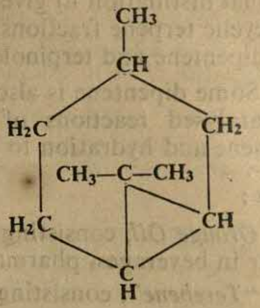
[1] The two rings do not lie in one plane, but in two planes almost perpendicular to each other.

[2] **Pinane** (b.p. 166°) does not itself occur in nature, but can be readily obtained from pinene by catalytic reduction.

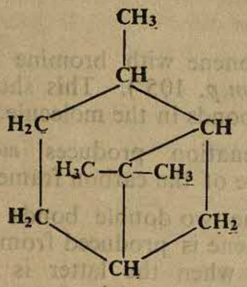
[3] **Turpentine oil** is obtained by steam distillation of resinous exudation of the various species of the pine tree. It may contain up to 90 per cent of pinene, and is mainly employed as a solvent in the manufacture of paints and lacquers.



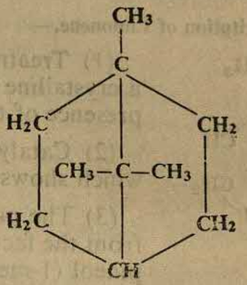
Thujane



Carane

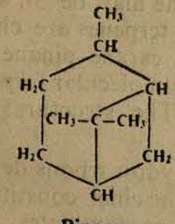


Pinane

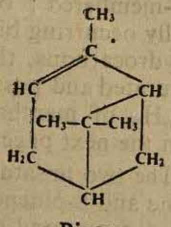


Camphane

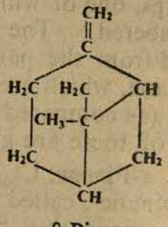
α- and the β- pinenes differ from each other in the position of the double bond (being 1,6- in the case of α- and 1,7- in that of β-). Their structural formulae, along with that of the parent hydrocarbon are given below :



Pinane



α-Pinene



β-Pinene

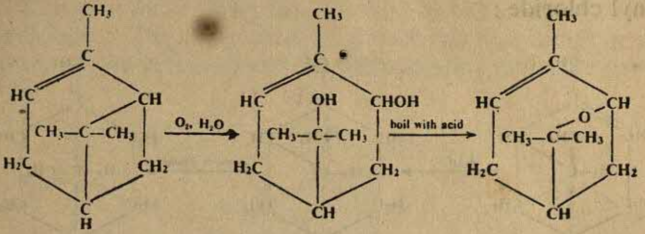
Properties.—

(1) α-Pinene boils at 156°. It occurs in nature in both the active and the inactive forms, the former being dextrorotatory, $[\alpha]_D = 48{\cdot}8°$.

(2) When exposed to air, pinene undergoes *autoxidation.* The first step in the process is the absorption of oxygen of the air to form

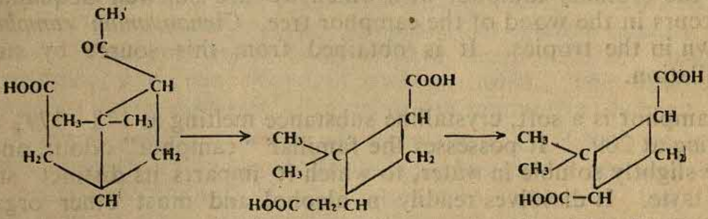
peroxides. These then break down into simple oxides with the setting free of some of the oxygen.

In the presence of moist air, **pinol hydrate** is formed as the result of oxidation, and separates out from the turpentine oil as crystals. When boiled with acids, pinol hydrate yields **pinol** :—



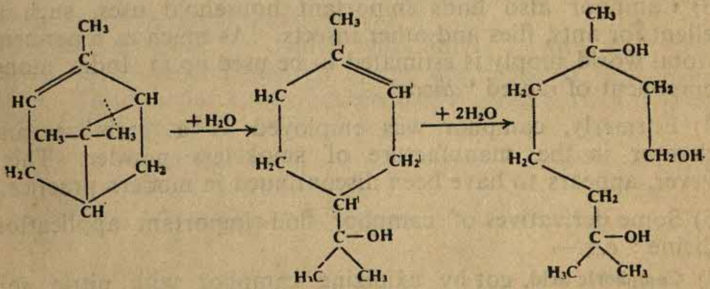
α-Pinene   Pinol hydrate   Pinol

(3) Oxidation of α-pinene by means of aqueous potassium permanganate attacks the double bond, and the carboxylic acids of the cyclobutane series, *viz. pinonic*, *pinic* and *norpinic* acids are successively produced :



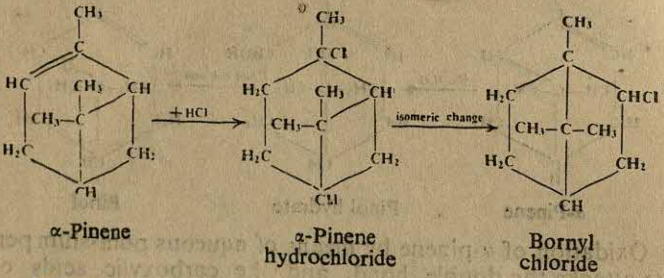
Pinonic acid   Pinic acid   Norpinic acid

(4) Treatment of α-pinene with dilute mineral acids results in the formation of α-terpineol and finally terpin hydrate. The terpineol formation involves addition of one molecule of water with the opening-up of the cyclobutane ring. The subsequent reaction involves opening-up of the cyclohexane ring and the disappearance of the double bond, two more molecules of water being thus added up.



α-Pinene   α-Terpineol   Terpin hydrate

(5) A reaction of considerable interest is the addition of dry hydrogen chloride. At very low temperatures, the reaction is a simple addition of HCl at the double bond, but, even at −10°, the α-pinene hydrochloride undergoes a remarkable isomeric change in which the 'bridged' linkage gets displaced from 2,4 to 1,4 position. The *pinane ring thus passes into the camphane ring* with the formation of bornyl chloride :



16. *d*-Camphor, $C_{10}H_{16}O$.— *d*-Camphor also known as *Japan camphor*, is the most important compound of the camphane group. It is the ordinary camphor with which we are so well acquainted. It occurs in the wood of the camphor tree, *Cinnamomum camphora*, grown in the tropics. It is obtained from this source by steam distillation.

Camphor is a soft, crystalline substance melting at 178—179° and boiling at 209°. It possesses the familiar "camphor" odour, and is only slightly soluble in water, to which it imparts its distinct smell and taste. It dissolves readily in alcohol and most other organic solvents.

Uses of Camphor.—

(1) Nowadays, the largest single use (about 80 per cent of the world supply) of camphor is in the manufacture of cellulose nitrate plastics (inclusive of photographic and cinema films).

(2) The second important use is in medicine, where it is employed in the form of ointment, tincture and liniment.

(3) Camphor also finds important household uses, such as a repellent for ants, flies and other insects. As much as 6 per cent of the total world supply is estimated to be used up in India alone as a component of sacred "*dhoop*".

(4) Formerly, camphor was employed as a stabilizer and a moderator in the manufacture of smokeless powder. This use, however, appears to have been discontinued in modern practice.

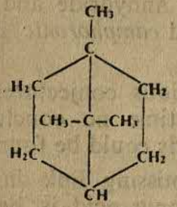
(5) Some derivatives of camphor find important application in medicine ; *e.g.*—

(*i*) **Camphoric acid**, got by oxidizing camphor with nitric acid, is used in compounding pharmaceutical preparations.

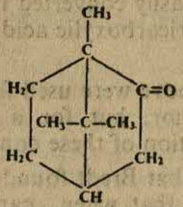
(*ii*) **β-Bromocamphor,** got by brominating camphor at its melting point, is used as a sedative and an antineuralgic.

(*iii*) **β-Camphorsulphonic acid,** obtained by sulphonation of camphor, employed as stimulant for respiration and blood circulation, in cases of heart failure, shock and poisoning by carbon monoxide, narcotics, etc.

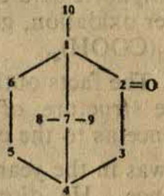
17. Constitution of Camphor.—Camphor has been shown to be is **2-camphanone** : The structures of camphane and camphor and the numbering of the carbon atoms in the camphor molecule are shown below :



Camphane



Camphor
(2-camphanone)



Numbering of carbon
atoms in camphor

The constitution of camphor was first correctly established by Bredt (1893). It is interesting to note that before Bredt's final solution of the problem as many as 30 or more different formulae for camphor had been proposed and discarded. The basic facts leading to the constitution of camphor are summarized below :

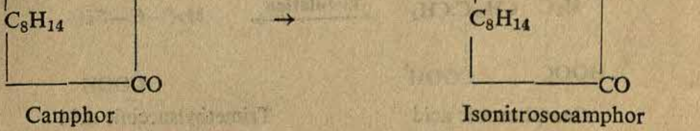
(1) The molecular formula of camphor is $C_{10}H_{16}O$. Its parent hydrocarbon therefore has the formula $C_{10}H_{18}$, which corresponds to the general formula C_nH_{2n-2}. Since it is unable to form any additive compounds, camphor, and its parent hydrocarbon, must be *bicyclic*. This view is further supported by the molecular refraction of camphor, which indicates that the molecule contains no double bonds.

(2) The functional nature of the oxygen atom is that of the keto group. This follows from the facts :

(*i*) Camphor reacts with hydroxylamine, to form *camphoroxime*, and with semicarbazide to form a semicarbazone.

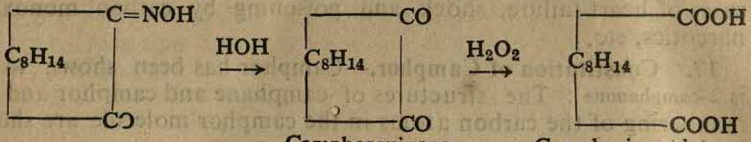
(*ii*) When reduced with sodium and alcohol, it gives the *secondary* alcohols, called *borneol* and *isoborneol*.

(3) When camphor is treated with amyl nitrite and sodium ethoxide, two of its hydrogen atoms are replaced by the group =NOH. This reaction is characteristic of compounds containing the —CH_2—CO— group.



Camphor Isonitrosocamphor

(4) Isonitrosocamphor, on hydrolysis, yields *camphorquinone*. This, when oxidized with hydrogen peroxide, gives *camphoric acid*, a dicarboxylic acid (which is also produced by oxidizing camphor with boiling nitric acid) :

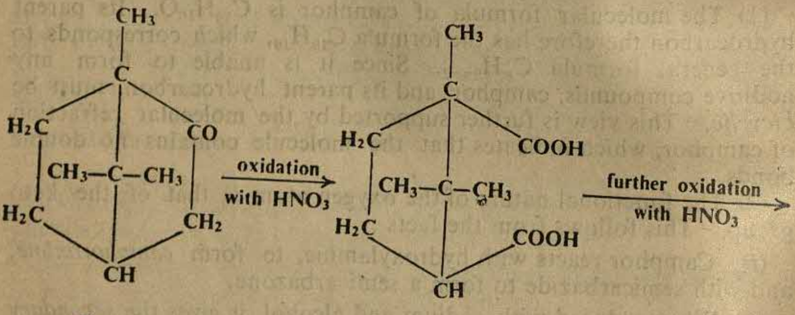


Camphorquinone Camphoric acid

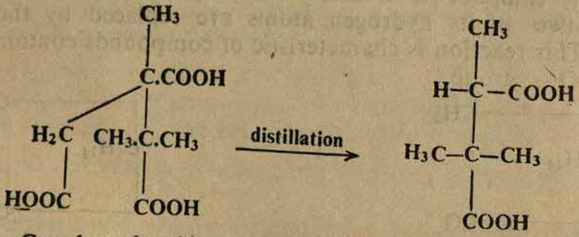
Camphoric acid can be easily converted into its anhydride and, on further oxidation, gives a tricarboxylic acid, called *camphoronic acid*, $C_6H_{11}(COOH)_3$.

(5) The facts outlined above were used for various conjectures as to the structure of camphor, but for a long time no conclusive evidence as to the constitution of these compounds could be found.

It was in the year 1893 that Bredt found the missing link in the evidence. He discovered that when camphoronic acid is heated slowly, it decomposes to give, isobutyric acid, trimethylsuccinic acid, carbon dioxide and carbon. From this observation and the facts already discovered by various investigators, Bredt was able to establish the structures of camphoronic acid, camphoric acid and camphor. A simplified scheme of the oxidative break-down of camphor and thermal decomposition of camphoronic acid is shown below :



Camphor Camphoric acid
(1,2, 2-Trimethyl -1, 3-cyclopentanedicarboxylic acid)



Camphoronic acid Trimethylsuccinic acid

Bredt's formula for camphor was accepted with reserve at the time it was proposed, but within the next ten years all his results and deductions were confirmed by the synthesis of camphoric acid by Komppa in 1903.

QUESTIONS

1. Write a short note on terpenes, giving their occurrence, chemical nature and classification.

2. Write structural formulae of menthane, 1-menthene and 1,8-menthadiene. Name at least one derivative of each of these hydrocarbons and write the structural formula in each case.

3. Give the occurrence. use and structural formula of each of the following compounds : (*i*) Citronellol, (*ii*) Geraniol, (*iii*) Citral.

4. Give the occurrence, synthesis (from thymol) and use of menthol.

5. What is *d*-limonene ? Give its occurrence and that of its optical isomers. Give the reasoning on which the structure of limonene is based.

6. Give an account of the analytical and synthetic evidence to elucidate the structure of citral. How is citral converted into ionones ?
(*Gujarat*, *B.Sc.*, *1958*)

7. What is heptenone ? Discuss its importance with respect to the chemistry of terpenes. How has this compound been synthesized ?

8. Discuss the geometrical isomerism of geraniol. How has the constitution of this compound been established ?

9. What is linalool ? How may it be obtained from (*i*) geraniol and (*ii*) methylheptenone ?

10. What is *p*-menthane ? What position does it occupy in the chemistry of terpenes ? Give illustrative examples in support of your views.

11. Give the structural formula, occurrence and uses of menthol. How has its constitution been established ?

12. What is menthone ? Give its occurrence and uses. How is it related to menthol ? Give structural formulae of the two compounds.

13. Give the occurrence, commercial preparation and uses of (*i*) *alpha*-terpineol and (*ii*) *d*-pulegone. How would you prove the constitution of *d*-pulegone ?

14. What is *limonene* ? How is it related to dipentene ? Give the occurrence, commercial sources and uses of limonene and dipentene. Discuss the constitution of limonene.

15. Give the occurrence and uses of *alpha*-pinene. Discuss its constitution. Give any *one* reaction of this compound involving the passage of the pinane ring to the camphane ring.

16. What is camphor ? What is it used for ? Discuss its constitution as fully as you can.

Appendix : Some Important Petrochemicals (refer to Sec. 24, page 188).—

Petrochemical	How obtained	Chief uses
(1) *From Methane* :		
Methyl alcohol	Synthesised from carbon monoxide and hydrogen	(*i*) Formaldehyde manufacture (*ii*) Antifreeze (*iii*) Solvent (*iv*) Chemical intermediate
Formaldehyde	Dehydrogenation of methyl alcohol	(*i*) Chemical intermediate (*ii*) Urea- and phenol-formaldehyde resins
Formic acid	From carbon monoxide and soda-lime so as to get sodium formate and decomposing the latter with equivalent quantity of sulphuric acid	(*i*) Textile industry (*ii*) Leather industry (*iii*) Resins and surface coatings (*iv*) Brewing industry and preservation of fruits (*v*) Chemical reagent
Methyl ether	From methanol by dehydration	(*i*) Low-temperature solvent (*ii*) Extracting agent (*iii*) Refrigerant for foodstuffs
Dimethyl sulphate	Interaction of methanol and sulphuric acid	(*i*) Methylating agent (*ii*) Dyes (*iii*) Pharmaceuticals
Ethylene glycol	Interaction of carbon monoxide and formaldehyde to produce glycolic acid and hydrogenating the latter	(*i*. Antifreeze in automobile and aeroplane radiators (*ii*) Solvent (*iii*) Chemical intermediate
Pentaerythritol	Condensation of formaldehyde with acetaldehyde	(*i*) High explosives (*ii*) Alkyd resins (*iii*) Plasticizers

Methyl chloride	(*i*) By chlorination of methane (*ii*) Esterification of methanol with HCl	(*i*) Methylating agent (*ii*) Refrigerant (*iii*) Solvent
Methylene chloride	By chlorination of methane or methyl chloride	(*i*) Chemical intermediate (*ii*) Refrigerant (*iii*) Industrial solvent
Chloroform	Chlorination of methane or methylene chloride	(*i*) Solvent for fats, waxes, resins, etc. (*ii*) Chemical intermediate (*iii*) Anaesthetic in surgery
Carbon tetrachloride	By chlorination of methane or chloroform	(*i*) Chemical intermediate (*ii*) Industrial solvent (*iii*) Fire extinguisher
Dichloromonofluoromethane	By fluorination of chloroform	Refrigerant
Dichlorodifluoromethane	Fluorination of carbon tetrachloride	Refrigerant
Methylamines (mono-, di- and tri-)	Action of ammonia on methanol	Chemical intermediate
Hexamethylenetetramine	Action of ammonia on formaldehyde	(*i*) Resins (*ii*) Pharmaceuticals
Hydrogen cyanide	Oxidation of methane-ammonia mixture	(*i*) Fumigant (*ii*) Chemical intermediate
Acetylene	Electric-arc treatment of methane	(*i*) Chemical intermediate (*ii*) Oxy-acetylene welding (*iii*) Illuminant
Acrylonitrile	Reaction between hydrogen cyanide and acetylene	(*i*) Synthetic fibres *ii*) Buna-N synthetic rubber
(2) •*From Ethane* :		
Ethylene	Pyrolysis of ethane	Chemical intermediate
Ethyl chloride	Chlorination of ethane	(*i*) Chemical intermediate

Petrochemicals	How obtained	Chief uses
		(*ii*) Tetraethyl-lead (*iii*) Refrigerant (*iv*) Solvent
Ethyl alcohol	From ethylene in two steps : (*i*) Absorption in conc. H_2SO_4 (*ii*) Hydrolysis of resulting $C_2H_5HSO_4$ with water	(*i*) Manufacture of acetaldehyde (*ii*) Solvent (*iii*) Chemical intermediate
Acetaldehyde	Dehydrogenation of ethyl alcohol	(*i*) Manufacture of acetic acid (*ii*) Chemical intermediate (*iii*) Resins
Acetic acid	Oxidation of acetaldehyde	(*i*) Manufacture of acetates (*ii*) Chemical intermediate (*iii*) Textile industry (*iv*) Coagulation of rubber latex
Acetic anhydride	Pyrolysis of acetic acid	(*i*) Manufacture of cellulose acetates (*ii*) Chemical intermediate
Ethyl acetate	(*i*) By esterification (*ii*) From acetaldehyde through Tischenko reaction ; *viz.*, condensation in presence of aluminium ethoxide as catalyst	(*i*) Fast-drying solvent for nitrocellulose (*ii*) Artificial leather manufacture (*iii*) Washable wall paper (*iv*) Flavours and perfumes (*v*) Synthetic dyes
Diethyl ether	Dehydration of ethyl alcohol	(*i*) Extracting agent (*ii*) Solvent (*iii*) Anaesthetic in surgery

(3) *From Propane* :

Ethylene	Pyrolysis of propane	Chemical intermediate
Dichloropropane (1,3-)	Chlorination of propane	Synthesis of cyclopropane
Nitromethane, nitroethane and nitropropanes	Vapour-phase nitration of propane gives a mixture of nitroparaffins	(*i*) Chemical intermediates (*ii*) Solvents
n-Propyl alcohol	Air-oxidation of propane-butane mixtures gives a mixture of aliphatics, from which *n*-propyl alcohol is separated	(*i*) Very good solvent for castor ; its largest use is in the manufacture of brake fluids (*ii*) Solvent for cellulose products, waxes and soaps (*iii*) Degreaser of metals and glass (*iv*) Chemical intermediate
Isopropyl alcohol	(*i*) From propylene by treatment with sulphuric acid followed by hydrolysis of isopropyl sulphate (*ii*) From propylene by catalytic hydration	(*i*) As a substitute of ethyl alcohol for many industrial purposes (*ii*) Manufacture of acetone (*iii*) Solvent for essential oils, resins, gums, shellac, etc., and is widely employed as such
Isopropyl ether	Obtained as a by-product of isopropyl alcohol manufacture	(*i*) Solvent (*ii*) Extracting agent (*iii*) Dewaxing of oils
Isopropylamines (mon- and di-)	Action of ammonia on isopropyl alcohol	(*i*) Chemical intermediate (*ii*) Leather processing
Acetone	Dehydrogenation of isopropyl alcohol	(*i*) Manufacture of acetic anhydride (*ii*) Solvent and extracting agent (*iii*) Chemical intermediate (*iv*) Storage of acetylene
Acetone cyanohydrin	Addition of HCN to acetone	(*i*) Chemical intermediate (*ii*) Manufacture of methacrylate resins

Petrochemicals	How obtained	Chief uses
(4) *From Butanes* :		
Butylenes (*n*- and *iso*-)	Dehydrogenation of butanes	See under Butylenes (p. 165)
Butadiene	Catalytic dehydrogenation of *n*-butane	See under Butadiene (p. 165)
'Alkylate'	Acid-catalysed condensation of isobutane and isobutene	100-Octane aviation petrol
Thiophene	Action of sulphur on *n*-buate	Chemical intermediate
(5) *From Pentanes* :		
Amyl chlorides	Chlorination of pentanes	(*i*) Chemical intermediates (*ii*) Solvents
Amyl alcohols	Hydrolysis of amyl chlorides	(*i*) Chemical intermediates (*ii*) Solvents (*iii*) Ore flotation
Amylamines	Treatment of amyl chlorides with ammonia	(*i*) Chemical intermediates (*ii*) Corrosion inhibitors
Amyl mercaptans	Treatment of amyl chlorides with NaHS	(*i*) Chemical intermediates (*ii*) Odorants
Pentylenes	By-products of hydrolysis of amyl chlorides	Chemical intermediates
Amylphenols	Interaction of pentylenes with phenol	(*i*) Chemical intermediates. (*ii*) Oil-soluble resins
(6) *From Ethylene* :		
Ethylene	Pyrolysis of ethane	Chemical intermediate

Ethyl alcohol	From ethylene in two steps : (*i*) Absorption in cold, conc. H_2SO_4 (*ii*) Hydrolysis of resulting $C_2H_5HSO_4$ with water	(*i*) Manufacture of acetaldehyde (*iii*) Solvent (*iii*) Chemical intermediate
Acetaldehyde	Dehydrogenation of ethyl alcohol	(*i*) Manufacture of acetic acid (*ii*) Chemical intermediate (*iii*) Resins
Acetic Acid	Oxidation of acetaldehyde	(*i*) Manufacture of acetone (*ii*) Chemical intermediate (*iii*) Textile industry (*iv*) Coagulation of rubber latex
Ethyl acetate	From acetaldehyde through Tischenko reaction	(*i*) Fast-drying solvent for nitrocellulose (*ii*) Artificial leather manufacture (*iii*) Washable wall paper (*iv*) Flavours and perfumes
Ethyl ether	Dehydration of ethyl alcohol	(*i*) Extracting agent (*ii*) Solvent (*iii*) Anaesthetic in surgery
Crotonaldehyde	From acetaldehyde by aldol condensation followed by dehydration	Chemical intermediate
Butraldehyde	Hydrogenation of crotonaldehyde	Chemical intermediate
n-Butyl alcohol	Reduction of butyraldehyde or of crotonaldehyde	(*i*) Chemical intermediate (*ii*) Solvent
Butyric acid	Oxidation of butyraldehyde	(*i*) Chemical intermediate (*ii*) Cellulose esters
Ethyl chloride	Catalysed addition of HCl to ethylene	(*i*) Tetraethyl-lead (*ii*) Solvent (*iii*) Refrigerant (*iv*) Chemical intermediate

Petrochemical	How obtained	Chief uses
Tetraethyl-lead	Action of Na-Pb alloy on ethyl chloride	Antiknock in automobile fuels
Ethylene dichloride	Addition of chlorine to ethylene	(*i*) Chemical intermediate (*ii*) Scavenger for tetraethyl-lead in motor fuels (*iii*) Fumigant
Ethylene dibromide	Addition of bromine to ethylene	(*i*) Chemical intermediate (*ii*) Scavenger for tetraethyl-lead
Ethylene chlorohydrin	Addition of hypochlorous acid to ethylene	Chemical intermediate
Ethylene oxide	Air-oxidation of ethylene in presence of silver-on-alundum catalyst	(*i*) Chemical intermediate (*ii*) Fumigant
Ethylene glycol	Hydrolysis with superheated steam	(*i*) Antifreeze in automobile radiators (*ii*) Explosives (*iii*) Chemical intermediate
Thiodiglycol	Interaction of ethylene oxide and H_2S	(*i*) Solvent in vat dye printing (*ii*) Mustard gas manufacture
Glyoxal	By oxidation of ethylene glycol	(*i*) Chemical intermediate (*ii*) Stabilization (directional) of rayon
Ethylene cyanohydrin	From ethylene oxide by addition of HCN	(*i*) Chemical intermediate (*ii*) Solvent
Acrylonitrile	Dehydration of ethylene cyanohydrin	(*i*) Fibres (*e.g.*, 'Orlon') (*ii*) Elastomers (*e.g*, 'Paracril')
Acrylic acid	Hydrolysis of ethylene cyanohydrin followed by dehydration of resulting hydracrylic acid	(*i*) Acrylic esters used in manufacture of high polymers (*ii*) Manufacture of plastics

(7) *From Propylene* :		
Isopropyl alcohol Isopropyl ether Isopropylamines (mono- and di-) Acetone Acetone cyanohydrin	See under Propane (p. 735)	
Diacetone alcohol	Condensation of acetone in presence of alkali	(*i*) Chemical intermediate (*ii*) Solvent
Mesityl oxide	Dehydration of diacetone alcohol	(*i*) Chemical intermediate (*ii*) Solvent
Ketene	Pyrolysis of acetone	Chemical intermediate
Acetylacetone	Condensation of acetone with ethyl acetate in presence of alkali	(*i*) Pesticides (*ii*) Metal salts used as pigments
Cumene (isopropylbenzene)	Interaction of propylene and benzene	(*i*) Chemical intermediate (*ii*) Solvent
Propylene oxide	Action of alkali on propylene chlorohydrin	(*i*) Chemical intermediate (*ii*) Solvent (*iii*) Preservative
Propylene glycol	Hydration of propylene oxide	(*i*) Chemical intermediate (*ii*) Solvent (*iii*) Pharmaceuticals (*iv*) Cosmetics
Polypropylene glycol ethers	Interaction of propylene oxide and alcohols	Lubricants
Propionaldehyde	Isomerization of propylene oxide	(*i*) Chemical intermediate (*ii*) Preservative (*iii*) Disinfectant

Petrochemicals	How obtained	Chief uses
Propionic acid	Oxidation of propionaldehyde	Chemical intermediate
n-Propyl alcohol	Reduction of propionaldehyde	(*i*) Chemical intermediate (*ii*) Solvent
Allyl chloride	Chlorination of propylene at high temperatures	Chemical intermediate
Allyl alcohol	Hydrolysis of allyl chloride	Chemical intermediate
Glycerol	From propylene in three steps : (*i*) Chlorination at 500° to form allyl chloride (*ii*) Treatment of the latter with hypochlorous acid to get glycerol dichlorohydrins (*iii*) Hydrolysis of these with alkali	(*i*) Nitroglycerin (*ii*) Alkyd resins (*iii*) Plasticizer
Acrlein	Catalytic oxidation of propylene	Chemical intermediate
(8) *From Butylenes :*		
Butyl alcohol (secondary)	Hydration of *n*-butylenes by absorption in sulphuric acid followed by treatment with water	(*i*) Chemical intermediate (*ii*) Solvent
Methyl ethyl ketone	Dehydrogenation of secondary butyl alcohol	Solvent
Ethyl butyl ketone	Aldol condensation of propionaldehyde with methyl ethyl ketone, followed by hydrogenation of the mixed product	Solvent

Butyl alcohol (tertiary)	Hydration of isobutylene	(*i*) Solvent (*ii*) Manufacture of lacquers
Polybutylenes	Polymerization of isobutylene	(*i*) Adhesives (*ii*) Plasticisers (*iii*) Electric insulation
Butyl rubber	Copolymerization of isobutylene and a small proportion of isoprene	Rubber goods
Iso-octane	Hydrogenation of di-isobutylene	High-octane motor fuels
(9) *From Diolefins* :		
Hexamethylenediamine	From butadiene in three steps: $CH_2=CH-CH=CH_2+Cl_2\rightarrow$ $CH_2Cl-CH=CH-CH_2Cl$ (treat with KCN)→ $CN.CH_2-CH=CH-CH_2CN$ (Hydrogenation)→ $NH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2$	Manufacture of Nylon
4-Vinylcyclohexene	Dimerization of butadiene	Chemical intermediate
Isoprene	From rectification of crude naphtha	(*i*) Synthetic rubber (*ii*) Drying oil modifier
(10) *From Acetylene* :		
Carbon black	Pyrolysis of acetylene	(*i*) Dry cells (*ii*) Rubber compounding
Vinylacetylene	Catalysed polymerization of acetylene	Chemical intermediate
Chloroprene	Addition of HCl to vinylacetylene	Neoprene elastomers
Acetaldehyde	Hydration of acetylene	See under Ethane (p. 752)
Acetic acid	Oxidation of acetaldehyde	

Petrochemical	How obtained	Chief uses
Peracetic acid	Acetylation of hydrogen peroxide by means of acetic acid in the presence of an acidic catalyst (1 per cent of H_2SO_4)	Very important organic oxidizing agent
Vinyl chloride	Addition of HCl to acetylene	(*i*) Plastics (*ii*) Synthetic fibres (*iii*) Chemical intermediate
Trichloroethane (1,1,2-)	Addition of chlorine to vinyl chloride	(*i*) Chemical intermediate (*ii*) Weed killer
Tetrachloroethane (1,1,2,2-)	Addition of chlorine to acetylene	Chemical intermediate.
Pentachloroethane	Addition of chlorine to trichloroethylene	Chemical intermediate
Ethylene dichloride	Reduction of tetrachloroethane	Solvent
Trichloroethylene	Dehydrochlorination of tetrachloroethane	(*i*) Chemical intermediate (*ii*) Solvent
Tetrachloroethylene	Dehydrochlorination of pentachloroethane	(*i*) Solvent (*ii*) Dry cleaning
Vinyl acetate	Addition of acetic acid to acetylene in presence of catalysts	(*i*) Plastics (*ii*) Synthetic fibres
Methyl vinyl ether	Addition of methyl alcohol to acetylene in presence of catalysts	(*i*) Chemical intermediate (*ii*) Polymers
Butadiene	Dehydration of 1,4-butanediol	(*i*) Synthetic rubber (*ii*) Surface coatings
Acrylonitrile	Addition of HCN to acetylene in presence of catalysts	(*i*) Chemical intermediate (*ii*) Synthetic fibres

(11) *From cycloalkanes* :		
Benzene	Dehydrogenation of cyclohexane	(*i*) Chemical intermediate (*ii*) Solvent
Toluene	Dehydrogenation of methylcycohexane	,, ,, ,,
Xylenes (*o*-, *m*- and *p*-)	Dehydrogenation of dimethylcyclohexane	,, ,, ,,
Adipic acid	Oxidation of cyclohexane	(*i*) Nylon manufacture (*ii*) Chemical intermediate
Hexamethylenediamine	From adipic acid in two steps: (*i*) Passing a mixture of the acid vapour and ammonia over thoria heated at 500°C, when adiponitrile is formed. (*ii*) Reduction of the nitrile	Nylon manufacture
(12) *From Toluene* :		
Benzyl chloride	Chlorination of toluene at 140° in presence of sunlight	(*i*) Chemical intermediate (*ii*) Drugs, dyes and resins
Benzal chloride	Chlorination of toluene	Manufacture of benzaldehyde
Benzotrichloride	,, ,,	(*i*) Manufacture of dyes (*e.g.* Malachite Green, Rosaniline, etc.) (*ii*) Manufacture of benzoic acid
Benzyl alcohol	Hydrolysis of benzyl chloride	(*i*) Pharmaceuticals and perfumery (*ii*) Chemical intermediate
Benzaldehyde	Hydrolysis of benzal chloride	(*i*) Beverage and food industry (as a flavouring agent and odorant) (*ii*) Manufacture of cinnamic aldehyde, benzyl benzoate, etc. (*iii*) Pharmaceuticals

Petrochemical	How obtained	Chief uses
Benzoic acid	Hydrolysis of benzotrichloride	(*i*) Preservative in fruit juices, crushed fruits, jams, jellies, pickles, etc. (*ii*) Inhibitor of rancidity and darkening of colour of oils. (*iii*) In dye industry, it is used in manufacture of Chrome Green, Spirit Blue, etc.
T.N.T.	Nitration of toluene	Explosive
Toluenesulphonic acids	Sulphonation of toluene	Chemical intermediate
p-Toluenesulphonamide	Dehydration of ammonium salt of *p*-toluenesulphonic acid	Chemical intermediates
Phthalic anhydride	Vapour-phase oxidation of *o*-xylene or naphthalene with air in presence of vanadium pentoxide (catalyst).	(*i*) Chemical intermediate (*ii*) Resin synthesis
Terephthalic acid	Vapour-phase oxidation of *p*-xylene	(*i*) Chemical intermediate (*ii*) Synthetic fibres (*iii*) Plasticizers

INDEX

Abel's flash-point apparatus, 183
Absolute alcohol, 243
Absorption spectra, 97
Acetaldehyde, 286
Acetanilide, 605
Acetoacetic acid, 417
Acetoacetic ester, 417
Acetone, 289
Acetonylacetone, 295
Acetophenone, 659
Acetyl value, 360
Acetylacetone, 295
Acetylene, 171
Acetylene dichloride, 213
    tetrachloride, 206
Acetylenic hydrocarbons, 168
Acid nitriles, 428
Acrolein, 291
Acyl groups, 300
Adipic acid, 386
Adjective dyeing, 628
Alamine, 468
Alcoholic fermentation, 240
Alcoholometry, 245
Alcohols, primary, secondary and tertiary, distinctive tests of, 235
Aldehyde ammonia, 273
Aldehydes and ketones, 265
Aldehydic acids, 417
Alicyclic compounds, 531
Alizarin, 699
Aldol condensation, 278
Alkaloids, 722
Alkanes, 132
Alkene oxides, 159
Alkenes, 152
Alkyl cyanides, 428
Alkyl halides, 194
Alkylate, 187
Alkylation of alkenes, 160
Alkylmagnesium halides, 215
Alkylsulphonic acids, 448
Alkylzinc halides, 221
Allyl alcohol, 248
    bromide, 212
    chloride, 211
    iodide, 211
    sulphide, 440
Alkynes, 168
Allylene, 563
Aluise's method of oxygen estimation, 38
Amethole, 644
Amine oxides, 457
Amines, 447
Amines, primary, preparation of, 451
Amines, primary, secondary and tertiary, separation of, 449
Amino acids, 461
Amino compounds, aromatic, 598
Aminoacetic acid, 467
Aminophenol, *para*, 643
Amyl alcohols, 247
Anethole, 644
Aniline, 602
Aniline Black, 605
Aniline Blue, 682
Aniline Yellow, 626
Animal charcoal, treatment with, 22
Anisole, 643
Anthracene, 695
Anthracene picrate, 695
Anthranilic acid, 666
Anthraquinone, 697
Antiknock compounds, 185
Aromatic acids, 662
Aromatic alcohols, 652
Aromatic aldehydes, 653
Aromatic halogen compounds, 579
Aromatic ketones, 558
Aromatic series, 539
Aromatic substitution, electronic theory of, 574
Aromatic sulphonic acids, 630
Aromatization of alkanes, 143
Aromatization of cyclohexane rings, 536
Arsonic acids, aromatic, 634
Aryl halides, 579
Ascent and descent of homologous series, 455
Aspartic acid, 469
Asymmetric synthesis, 116
Atoxyl, 633
Atropine, 728
Aurin, 683
Auxochromes, 623
Aviation gasoline, 186
Azeotropic distillation, 243
Azo dyes, 622, 624
Azobenzene, 621
Azoxybenzene, 621

Bakelite, 285, 641
BAL, 438
Barbituric acid, 384, 475
Bayer's strain theory, 69
Beckmann's apparatus, 5
Beilstein's test, 31
Benedict's reagent, 492
Benzal chloride, 585

Benzaldehyde, 654
Benzamide, 666
Benzanilide, 605
Benzene, 546
Benzene, homologues of, 558
Benzene hexachloride, 586
Benzene-*m*-disulphonic acid, 633
Benzenesulphonic acid, 632
Benzoin condensation, 656
Bezoquinone, 649
Benzyl alcohol, 652
Benzyl chloride, 585
Benzylamine, 612
Benzoic acid, 663
Benzoic anhydride, 666
Benzophenone, 659
Benzoyl chloride, 665
Bergius process for coal hydrogenation, 190
Betaine, 469
Bis-azo dyes, 627
Bismarck brown, 626
Biuret, 413
Blasting gelatine, 355
Blue-black ink, 674
Boiling point, determination of, 25
Bomb furnace, 42
Bouveault-Blanc reduction, 228
Bromobenzene, 583
Bromoform, 203
Brucine, 731
Butadiene, 165
Butter substitutes, 361
Butyl alcohols, 246

Cacodyl compounds, 440
Caffein, 481
Camphor, 746
Camphoric acid, 746
Cane-sugar, 513
Cannizaro's reaction, 279, 655
Carbinol, 224
Carbitols, 348
Carbohydrates, 485
Carbon suboxide, 380
Carbolic acid, 638
Carbon tetrachloride, 205
Carbonic acid, 409
Carbonic esters, 410
Carbonyl chloride, 409
Carbonyl group, reactions of, 271
Carbylamine reaction, 601
Carbylamines, 430
Carius' method of halogen estimation, 42
Carvacrol, 644
Catechol, 644
Cellobiose, 520
Cellosolves, 348
Celluloid, 529
Cellulose, 525
Ceresin, 189
Chloral, 288
Chloral hydrate, 288
Chlorex, 263
Chloroacetic acids, 341
Chlorocarbonic acid, 410
Chloroform, 202
Chlorobenzene, 582
Chlorotoluene, 584
Chromogens, 623
Chromatography, 20
Chromophores, 623
Chrysoidine, 626
Cinchomeronic acid, 710
Cinchonine, 730
Cinnamic acid, 675
Cinnamic aldehyde, 657
Cinnamyl alcohol, 652
Cis-trans isomerism, 119
Citric acid, 403
Citral, 734
Claisen's condensation, 676
Claisen's reaction, 280, 656
Cocaine, 728
Coal-tar distillation, 540
Coal-tar industry in India 545
Coffey still, 241
Colour and constitution, relation between, 622
Cambustion furnace, 33
Condensation, 281
Congo red, 627
Coniine, 723
Conjugated double bonds, 73
Co-ordinate link, 77
Cordite, 355
Coumarin, 677
Coumarinic acid, 677
Coupling reactions, 618
Cracked gasoline, 186
Creosote oil, 543
Cresols, 644
Crotonaldehyde, 292
Crum Brown-Gibson rule, 571
Cyanic acid, 431
Cyanogen, 425
Cyanogen compounds, 425
Cyanuric acid, 431
Cyclanes, 531
Cycloalkanes, 531
Cyclohexane, 537
Cyclonite, 284
Cyclopentane, 537
Cymene, 563

D.D.T., 584
Decalin, 692
Dennstedt's method of carbon-hydrogen estimation, 37
Detection of elements in organic compounds, 29
Detergents, 368
  action of, 369

Detergents, higher quaternary salts as, 457
Diacetyl, 293
Diacetylene, 176
Dialkenes, 165
Dialysis, 18
Diaminobenzene, 609
Diazoaminobenzene, 619
Diazonium salts, 615
Diazonium salts, uses of, 619
Diazotization, 615
Dicarboxylic acid, 373
Dichloroacetic acid, 341
Diels-Alder condensation, 165
Diels-Alder reaction, 533, 548
Diethyl ether, 260
Diethyl sulphate, 254
Dihydric alcohols, 343
Dimethyl sulphate, 254
Dimethylamine, 455
Dimethylaniline, 611
Dimethylglyoxime, 294
Dinitobenzene, 593
Dioxane, 349
Dioxindole, 713
Dipentene, 742
Diphenyl, 679
Diphenylamine, 610
Diphenylmethane, 679
Dipole moments, 98, 575
  and molecular structure, 100
Dipole moments of amino acids, 463
Directive influence of substituents, 569
Disaccharides, 512
Disacryl, 292
Distillation under reduced pressure, 15
Distribution law, 20
Drying of organic compounds, 22
Drying oils, 370
Dumas' method of decarboxylation of acids, 138
Dumas' method of nitrogen estimation, 39
Dumas' method of vapour density determination, 48
Durite, 641
Dyeing, 628
Dynamite, 355

Effectiveness of directing groups, 569
Elaidinization, 363
Electronic theory of aromatic substitution, 574
Electronic theory of valency, 76
Electrophilic reactions, 576
Electrovalency, 76
Enzyme catalysis, 128
  kinetics of, 130
  nature of, 130
Eosin, 684
Epimerization of aldoses, 493
Esters of inorganic oxy-acids, 252
Estimation of elements in organic compounds, 33
Etard reaction, 654
Ethane, 149
Ether, amyl, 263
  butyl, 263
  ethyl, 260
  isopropyl, 263
  methyl, 263
  vinyl, 263
Ethers, 257
Ethyl acetoacetate, 417
Ethyl alcohol, 239
Ethyl bromide, 200
Ethyl chloride, 199
Ethyl ether, 260
Ethyl fluid, 221
Ethyl hydrogen sulphate, 253
Ethyl iodide, 201
Ethyl mercaptan, 437
Ethyl nitrate, 254
Ethylene, 162
Ethylene chlorohydrin, 347
Ethylene dibromide, 202
Ethylene glycol, 344
Ethylene oxide 347
Ethylenic double bond, detection of, 160
  estimation of, 161
Exhaustive oxidation, 159
Explosives, 527, 596
Extraction with solvents, 19

Fats and fatty oils, 358
Fehling's reagent, 492
Fischer-Tropsch process for synthetic petrol, 192
Flash point, 183
Fluorescein, 684
Fluoro derivatives of hydrocarbons, 207
Fluorocarbons, 207
Formal titration, 465
Formaldehyde, 282
Formalin, 283
Fractional crystallization, 9
Fractional distillation, 13
  industrial, 15
  under reduced pressure, 16
Freiedel-Crafts' hydrocarbon synthesis, 558
Freons, 207
Fructose, 509
Fumaric acid, 387
Furan, 703
Furfural, 703
Furfuraldehyde, 703
Fusel alcohol, 243

Galalith, 285
Gallic acid, 673
Gasoline, manufacture of, 184

Gattermann's reaction, 617
Geneva system of nomenclature, 135
Geometrical isomerism, 118
Geraniol, 737
Glucose, 501
  constitution of, 504
  cyclic structure of, 505
Glutamic acid, 469
Glutaric acid, 386
Glycerides, 358
Glycerine, 349
Glycerol, 349
Glycerophosphates, 352
Glycerose, 352
Glycine, 467
Glycolic acid, 397
Glycols, 343
Glyoxal. 291
Green oil, 544
Grignard reagents, 215

Halogen derivatives of aliphatic hydrocarbons, 194
Halogen-substituted monocarboxylic acids, 339
Hammick-Illingworth rule, 571
Hardening of fats and oils 362
Hexamethylene tetramine, 284
Hodgson and Marseden's method, 617
Holoform reaction, 204
Homologous series, 66
Hydrobenzamide, 656
Hydracrylic acid, 400
Hydrazobenzene, 622
Hydrogen bonding in enol-acetoacetic ester, 422
Hydrogen cyanide, 426
Hydrocyanic acid, 426
Hydrogenated naphthalenes, 692
Hydrogenation of alkenes, 156
Hydroxycarboxylic acids, 393
Hydroxylation of alkenes, 158
Hydroxyquinol, 648
Hypoxanthine, 481
Hydroxycinnamic acid, 676

Ingrain dyeing, 628
Iodine value, 360
Iodobenzene, 582
Indigo, 714
Indigo, natural, 714
Indole, 712
Inodophenine, 714
Indoxyl, 713
Indoxylic acid, 713
Iodoform, 204
Isobutyl alcohol, 246
Isocyanides, 430
Isatin, 714
Isoelectric point, 463
Isomerism, 63
  chain, 66
  nuclear, 66
  position, 66
Isonitriles, 430
Iso-octane, 184
Isoquinoline, 720
Isoprene, 166
Isopropyl alcohol, 245
Ittner's process of countercurrent hydrolysis, 364
I.U.C. system of nomenclature, 132

Kekule and Couper's theory, 63
Kerosene oil, 183
Ketonic acids, 417
Ketonic hydrolysis, 419
Kjeldahl's method of nitrogen estimation, 41
Knoevenagel reaction, 280
Kolbe's reaction, 137
Kolbe-Schmitt reaction, 671
Korner's method of orientation, 567

Lacquers, 529
Lactic acid, 397
Lactic acids, isomerism of, 107
Lactose, 520
Lamp-black, 144
Lassaigne's test, 29, 31
Le Bel and van't Hoff's theory, 107
Leucine, 469
Lewisite, 441
Light oil, 541
Linalool, 739
Lindane, 586
Lobry de Bruyn transformation, 493

Malachite Green, 679
Maleic acid, 387
Malonic acid, 379
Malonic ester, 380
Malonic ester syntheses, 381
Maltose, 519
Mandelic acid, 675
Meerwein-Ponndorf reduction, 228
Melting point, determination of, 24
Menthane, 740
Menthanol, 740
Menthanone, 741
Menthenes, 742
Mercaptans, 435
Mesityl oxide, 280
Mesitylene, 563
Metaldehyde, 277
Meta orientation, 577
Metamerism, 67
Methane, 146
Methonine, 212
Methyl alcohol, 236
  bromide, 199
  chloride, 199
  iodide, 200
  salicylate, 673

Methyl orange, 627
Methylamine, 455
Methylaniline, 611
Methylheptenone, 737
Methylmagnesium iodide, preparation of, 216
Methylxanthine, 481
Michler's ketone, 660
Middle oil, 543
Milk-sugar, 520
Molecular formulae, determination of, 46
  of acids, 58
  of bases, 59
  of gaseous hydrocarbons, 54
Molecular weight determination, 49
  boiling point method, 52
  freezing point method, 49
  of non-volatile substances, 49
  of volatile substances, 47
  Rast's method, 51
  Victor Meyer's method, 47
Molisch's test, 492
Monocarboxylic acids, 299
Monochloroacetic acid, 341
Monohydric alcohols, 224
Monocyclic monoterpenes, 740
Monosaccharides, 485
  classification of, 485
  configuration of, 496
  physical properties of, 486
  reactions of, 486
Morphine, 731
Mustard gas, 439
Mutarotation, 506
Myrcene, 733

Naphthalene, 686
Naphthalene carboxylic acids, 692
Naphthalenesulphonic acids, 690
Naphthaquinones, 692
Naphthol orange, 627
Naphthols, 691
Naphthylamines, 691
Natural gas, 189
Neoprene, 168
Nicotine, 726
Nitranilines, 608
Nitration of alkanes, vapour phase, 145
Nitro compounds, 443
Nitro compounds, aromatic, 588
Nitrobenzene, 592
Nitroglycerine, 354
Nitroglycol, 346
Nitrolic acids, 235
Nitronaphthalenes, 690
Nitroparaffins, 443
Nitroparaffins and alkyl nitrites, distinctive properties of, 445
Nitrophenols, 641
Nitrotoluenes, 594
Nucleophilic reactions, 576
Nylon, 386

Ocimene, 734
Octane number, 184
Oil-gas, 188
Oil of wintergreen, 673
Olefins, 152
Oleo-margarine, 361
Optical activity, 88
  antipodes, 110
  enantiomorphs, 107
  inversion, 117
  isomerism, 399
Orcinol, 646
Organic and inorganic chemistry, main differences between, 2
Organic chemistry in service of chemical industry, 4
Organometallic compounds, 215
Orienting influence of substituents, 576
Orientation of substituents, 566
Ornithine, 469
Ortho-para orientation, 576
Orthoaldehydes, 272
Orthoketones, 272
Osazone formation, 489
Oxalic acid, 376
Oxindole, 713
Ozokerite, 189
Ozonide formation, 159
Ozonolysis, 159

Paper manufacture, 526
Parachor, 82
Paraffin hydrocarbons, 132
Paraformaldehyde, 283
Paraldehyde, 283
Pentaerythritol, 355
  tetranitrate, 355
P.E.T.N., 355
Perfluorohexane, 207
Perkin's reaction, 280, 675
Petrochemicals, 188, 750
Petroleum industry, 179
Phenanthraquinone, 701
Phenanthrene, 701
Phenetole, 643
Phenolic acids 669
Phenolic aldehydes, 657
Phenolphthalein, 683
Phenylacetic acid, 675
Phthaleins, 683
Phthalic acid, 667
Phthalic anhydride, 668
Phthalimide, 669
Phthalyl chloride, 669
Phenol-formaldehyde resins, 641
Phenols, 636
Phenyl salicylate, 673
Phenylenediamines, 609
Phenylhydrazine, 621
Phenylhydrazones, 274

Phenylnitromethane, 597
Phloroglucinol, 647
Phorone, 280
Photochlorination, 141
Physical properties and chemical constitution, 82
Picrates, 642
Picric acid, 642
Pinene, 743
Piperidine, 710
Piperine, 725
Piperonal, 658
Pitch, 544
Polarimetry, 89
Polyisobutylene, 165
Polyhydric alcohols, 343
Polymerization, 281
Polyphenyl, 679
Polyphenyl compounds, 679
Polythene, 164
Prestone, 347
Propane, 151
Propargyl alcohol, 249
        bromide, 213
Propyl alcohol, 245
Propylene, 165
Proteins, 470
    constitution of, 473
Protocatechuic aldehyde, 658
Pseudonitrols, 235
Pulegone, 742
Purification of organic compounds, 7
    chemical methods, 23
Purines, 475
Purity of a substance, methods of testing, 24
Pyridine, 708
Pyridinecarboxylic acids, 710
Pyragallol, 646
Pyrogallic acid, 646
Pyranose formula of glucose, 508
Pyromucic acid, 704
Pyrrole, 706

Qualitative elementary analysis, 28
Quantitative elementary analysis, 33
Quinhydrone, 651
Quinine, 729
Quinoline, 717
Quinone, 649
Quinones, 649
Quinonoid compounds, 650
Quinol, 646

Racemic compounds, significance of, 112
    resolution of, 114
Racemization, 111
Raman spectra, 464
Rancidity, 361
Raney nickel, 227
Rast's method, 51
Reichert-Meisel value, 360
Resonance, 79
Resonance in benzene ring, [illegible]
Resorcinol, 646
Rimini's test, 285
Rosaniline, 681
Rosenmund reduction, 265
Rosolic acid, 683
Rotation
    magnetic, 91
    molecular, 91
    specific, 90
Rotatory dispersion, 110
Rubber, 165
    buna, 167
    butyl, 167
    natural, 166
    polysulphide, 168
    synthetic, 167
Ruff degradation, 494

Saccharin, 667
Sachse Mohr theory, 71
Salicyl alcohol, 653
Salicylaldehyde, 657
Salicylic acid, 670
Saligenin, 653
Salting out, 21
Salvarsan, 635
Sandmeyer's reaction, 617
Saponification value, 359
Saturated hydrocarbons, 132
Schiff's reaction, 281
Selivanoff's test, 492
Semicarbazones, 274
Semipolar double bond, 79
Shale, 189
Silk, artificial, 527
Siwolowoff's method of boiling-point determination, 26
Skaolte, 713
Skraup's synthesis of quinoline, 718
Soaps, 366
    cation-active, 368
Soda-lime test, 30
Sodium salicylate, 673
Starch, 522
Steam distillation, 17
Stereochemistry, 104
    of nitrogen, 120
Steric hindrance, 122
Strain theory, 68
Strainless multiplanar rings, 71
Strainless theory, 71
Structural formula, determination of, 74
Strychnine, 730
Styrene, 564
Sublimation, 10
Substitution, 65
Succinic acid, 385
    deterivatives of, 386
Sucrose, 513

Sulphanilic acid, 605
Sulphanilamide, 607
Sulphonal, 437
Sulphonation of aromatic compounds, 630
Synthetic petrol, 190
Tannic acid, 674
Tannins, 674

Tartaric acid, 401
  optical isomerism of, 403
Tartaric acids, Pasteur's work on, 104
Tautomerism, 75
Ter Meulen's method of halogen estimation, 42
Ter Meulen's method of nitrogen estimation, 42
Ter Meulen's method of oxygen estimation, 38
Terpenes, 733
Terpineol, 742
Tetraethyl lead, 221
Tetramethylammonium hydroxide, 455
Tetranitromethylaniline, 596
Theine, 481
Theobromine, 483
Thermoplastic resins, 641
Thermosetting resins, 641
Thiele's theory of partial valency, 73
Thio-alcohols, 435
Thio-ethers, 438
Thiokol, 168
Thiols, 435
Thiophene, 705
Thymol, 644
Tischenko reactions, 279
Titer test, 360
Toluene, 561
Toluic acids, 667
Toluidines, 608
Tricarboxylic acids, 403
Trichloroacetic acid, 341
Trimethylamine, 455
Trimethylglycine, 468
Triphenylamine, 610
Triphenylmethane, 679
Triphenylmethane dyes, 679
Triphenylrosaniline, 682
Twitchell's process, 365

Ullmann's reaction, 581
Unsaturated dibasic acids, 387
Unstaurated hydrocarbons, 152
Urea, 411
Ureides, 475
Uric acid, 476

Valency, electronic theory of, 6
Vanillin, 658
Vat-dyeing, 717
Vegetable oils, refining of, 362
Veronal, 384, 475
Victor Meyer's method of distinguishing between primary, secondary and tertiary alcohols, 234
Victor Meyer's method of molecular weight determination, 47
Vinyl acetate, 248
  bromide, 211
  chloride, 211
  ether, 263
  esters, 247
  resins, 248
Viscose silk, 528
Vorlander's rule, 571

Walden inversion, 117
Westron, 206
Westrosol, 213
Witt's theory, 622
Wohl degradation, 494
Wurtz-Fittig reaction, 581

Xanthine, 481
Xylene, 562

Zinc alkyls, 220
  diethyl, 220
Zwitterion structure of sulphanilic acid, 606
Zwitterion structure of amino acids, 462

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